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Vol. LVI MAY 1961 No. 5

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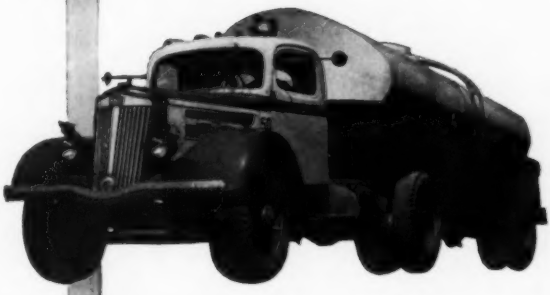

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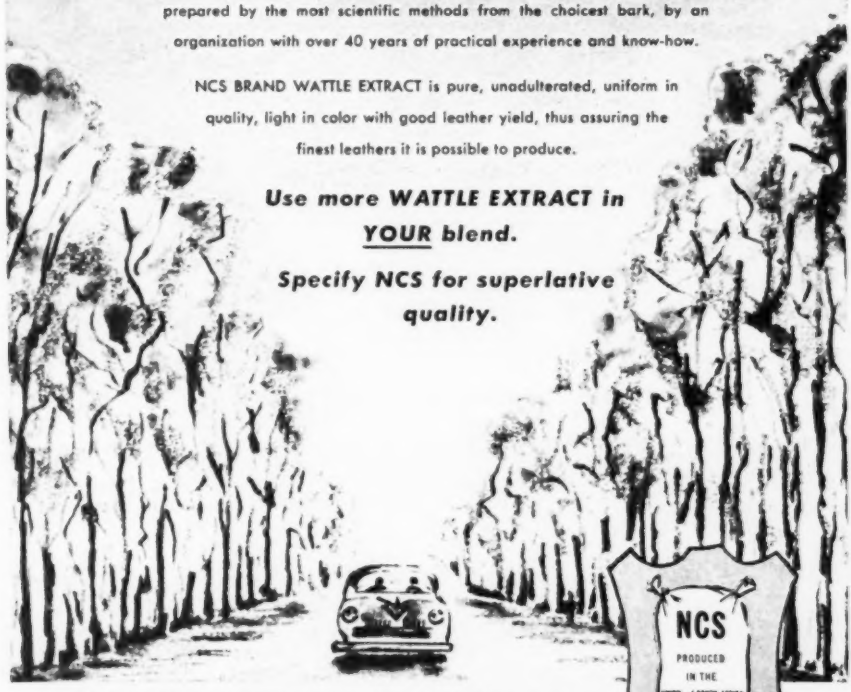

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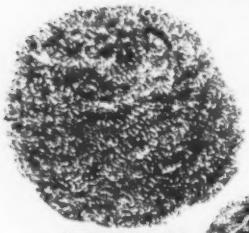

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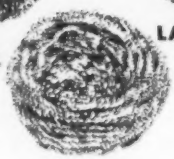

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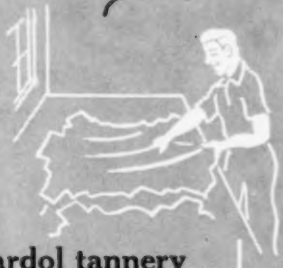

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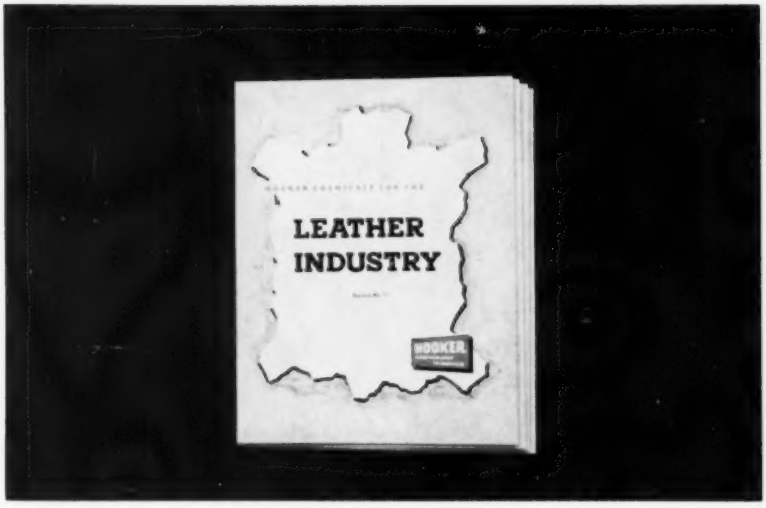

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General correspondence concerning the *Journal* should be mailed to the Managing Editor.
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TANNING STUDIES WITH DIALDEHYDE STARCH

PRELIMINARY EVALUATION OF THE LEATHER*

E. M. Filachione, I. D. Clarke, E. H. Harris, Jr., J. Fee,

L. P. Witnauer, and J. Naghski

Eastern Regional Research Laboratory†
Philadelphia 18, Pennsylvania

and

J. N. Boyd

Biometrical Services, ARS
Beltsville, Md.

ABSTRACT

Calfskin (acetone-dehydrated) was tanned with dialdehyde starch under various conditions. Four tanning variables were investigated. These were: (*a*) dialdehyde starch of three oxidation levels, i.e., 33, 67, and 96%; (*b*) two pH levels, i.e., 8 and 10; (*c*) two methods for dissolving the dialdehyde starch; and (*d*) oiling the leather. The experiments were designed statistically. Tanning with dialdehyde starch, oxidized to the 96% level, at pH 10 and oiling the leather in general resulted in the optimum leather properties and characteristics for this tannage.

—×—×—

INTRODUCTION

Previous publications from this laboratory (1, 2, 3) reported that dialdehyde starch, also referred to as periodate oxystarch or simply oxystarch, was found to effect a tanning action. Dialdehyde starch is a polyfunctional aldehyde derived from ordinary starch by oxidation with periodic acid. The extent of oxidation can be controlled to provide a complete range of aldehyde derivatives of starch in which the level of oxidation varies from 0% to 100%. Our interest in dialdehyde starch was stimulated by recent developments in its preparation (4, 5, 6) which offer promise of making this polyaldehyde commercially available (7, 8).

*Presented in part at the Fifty-third Annual Meeting of the American Leather Chemists Association, Lake Placid, New York, June 2–5, 1957.

†Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

Our previous study (2) was primarily concerned with demonstrating the tanning power of dialdehyde starch. Data on the physical properties of leather obtained from this unusual aldehyde were desirable, and a preliminary evaluation of the leather and correlation with certain tanning variables are reported in this study. This series of tests was made using starch oxidized to three levels, i.e., 33, 67, and 96%. For convenience these dialdehyde starch preparations may be referred to as DAS-33, DAS-67, and DAS-96 respectively. Leffler and Stanko (8) in a recent publication have used the abbreviation "DAS" for dialdehyde starch. The dialdehyde starches were dissolved by two methods, described below, and were used at two pH levels, namely, 8 and 10. The leathers were examined in the unoiled as well as the oiled condition; hence 24 treatments were involved. For convenience, and to facilitate area and thickness measurements, acetone-dehydrated calfskin was used.

EXPERIMENTAL

Hide material.—Five pickled calfskins, weighing between 9 and 12 lb. each, were obtained from a tannery. These were depickled in a laboratory drum with 200% (based on the drained, pickled weight) of a solution 5% with respect to both sodium chloride and anhydrous sodium acetate. After being drummed for 3 hr., at which time the pH was 5.1, the skins were thoroughly washed, drained, and dehydrated by immersion in several changes of acetone. The skins, after being blotted on towels, were tacked out and covered with towels, and the acetone was permitted to evaporate slowly. All manipulations involving acetone were carried out in a fume cupboard. The acetone-dehydrated skins were cut into sides, and each of the 10 sides was cut into 3 strips, 3.25″ in width. Each strip was then divided into 8 squares (3.25″ x 3.25″) for a total of 24 squares from each side. Tanned pieces approximately 3″ square were required for testing, so it was necessary to cut larger pieces from the raw skin to allow for shrinkage during tanning. The squares from each of the 10 sides were assigned at random to 24 piles or lots, and one lot was then assigned at random to each of the 24 treatments. Pilot pieces from the edges of the skins were included with each lot in order to follow the progress of tanning. Before the tanning, the squares were conditioned at 50% relative humidity and 73°F.; then they were subjected to measurements of area, weight, and thickness. For the actual tanning, lots 1 and 13, 2 and 14, etc., were combined. After the tanning, the squares assigned to lots 1 to 12 inclusive were removed from the respective combined lots, and the remaining squares, comprising lots 13 to 24 inclusive, were fatliquored.

Dialdehyde starch tannage.—Dialdehyde starches of oxidation levels corresponding to 33, 67, and 96% were obtained from the Northern Utilization Research and Development Division. They were prepared for tanning

TABLE I

EFFECT OF TANNING VARIABLES ON DIALDEHYDE STARCH-TANNED CALFSKIN

Lot or Tannage No.	Oxidation of Starch %	Method of Dissolving Starch*	pH of Tan Liquor	Ts °C.†	Finishing	Grade	Area Yield %	Weight Yield %	Thickness Yield %	Stiffness E Kg/cm²	Leather Quality
1	33	a	8	77	No oil	1.0	84	110	76	4780	hard, stiff, untanned
2	33	b	8	76	"	1.2	89	111	77	3930	tinny, undertanned
3	33	a	10	89	"	3.0	99	110	80	1430	stiff, thin, poor
4	33	b	10	88	"	3.0	94	110	88	1040	stiff, thin, poor
5	67	a	8	77	"	1.4	98	113	90	1880	tinny, undertanned
6	67	b	8	79	"	2.0	95	114	92	1660	tinny, undertanned
7	67	a	10	84	"	2.5	95	111	85	1140	poor, some tinny pieces
8	67	b	10	86	"	4.1	99	111	84	940	flat, nonuniform color
9	96	a	8	82	"	3.9	90	112	97	1090	fairly well tanned
10	96	b	8	83	"	3.7	96	111	97	1400	some good pieces; some thin
11	96	a	10	85	"	4.8	92	108	95	910	well tanned, good feel
12	96	b	10	89	"	4.2	91	109	96	580	well tanned, good feel
13	33	a	8	72	Oiled	1.3	92	117	87	1100	flat, tinny, undertanned
14	33	b	8	72	"	2.4	97	118	81	830	flat, tinny, undertanned
15	33	a	10	89	"	4.3	100	122	87	420	fair, rather thin
16	33	b	10	82	"	4.1	104	123	89	360	well tanned, mellow
17	67	a	8	78	"	3.1	102	122	87	530	fair, rather thin and firm
18	67	b	8	78	"	4.1	101	124	96	610	not well tanned
19	67	a	10	84	"	3.7	97	118	88	390	not well tanned
20	67	b	10	84	"	4.4	100	119	89	320	well tanned, mellow
21	96	a	8	80	"	4.4	91	121	103	350	good feel, variable firmness
22	96	b	8	79	"	4.4	93	118	99	490	good feel, slightly firm
23	96	a	10	77	"	4.6	93	118	103	240	good feel, well tanned
24	96	b	10	84	"	4.9	90	117	100	240	good feel, well tanned

* *a* = heating in autoclave; *b* = solid starch added to alkaline tan liquor.
† Ts for lots 1–12 were taken at the end of the 24-hr. tannage; Ts of lots 13–24 were taken after the tanned skins were brought to pH of about 4. Generally there was a drop in Ts upon acidification of these alkaline tannages.

by two procedures. In one series the dialdehyde starch (DAS) was dissolved by heating a dilute aqueous suspension in an autoclave. This method will be referred to hereafter as Method A. In a second series, Method B, the solid DAS was added to, and allowed to dissolve in, the alkaline tan liquor during the tanning process. Details of the tanning are given below. A summary of the tanning conditions for each of the 24 lots is shown in Table I.

Method A.—In this procedure the DAS was first dissolved by autoclaving an aqueous suspension at 120°C. for 30 minutes. A 16% suspension of DAS-33 and 10% suspensions of DAS-67 and DAS-96 were autoclaved.

The lots of acetone-dehydrated calfskin squares to be given the identical tannage were combined, rehydrated in running tap water for 2 hr., and then put through a wringer. Based on the wrung weight the amount of DAS, on a moisture-free basis, taken for tanning was 10, 15.5, and 29% for the levels of oxidation corresponding to 96, 67, and 33% respectively. To the DAS solution prepared by autoclaving was added 26% anhydrous sodium sulfate and 4.5% sodium bicarbonate, each based on the wrung weight of the lots of calfskin, and sufficient water to make a 2:1 float. The wrung skin pieces were then added, and tanning was carried out in vented bottles with agitation provided by rolling the bottles on their sides.

The tanning was carried out for 24 hr., and the pH at the end was in the range of 7.0 to 7.8. Tanning at pH of about 10 was conducted in the same way except that 2.7% of magnesium oxide in addition to the 4.5% sodium bicarbonate was used. The pH at the end of the 24-hr. tannage was in the range of 9.4 to 9.9. The shrinkage temperatures are shown in Table I (Method A, lots 1–12).

At the end of the 24-hr. tannage, the pieces were washed briefly and then brought to a pH of about 4 by agitation in a 1% acetic acid solution. The pieces were then thoroughly washed and wrung. Ts after acidification is listed in Table I (Method A, lots 13–24).

The pieces to be oiled were removed and fatliquored by the method to be described later, then all were dried in air.

Method B.—In this procedure the solid DAS was added to the skins in an alkaline liquor. Under these conditions the solid DAS dissolved gradually, and tanning was effected by the resulting solution. Details are essentially as follows:

The combined lots of acetone-dehydrated calfskin squares were rehydrated by immersion in water for 2 hr. and then wrung. Based on the wet wrung weight the amount of DAS (MFB) taken for tanning was 10, 15.5, and 29% for the three different oxidation levels, as was done under Method A above. An aqueous solution was prepared from 27% anhydrous sodium sulfate and 4.5% sodium bicarbonate (based on wrung weight) in enough water to make

a 2:1 float. The wrung calfskin squares were then added, and the appropriate amount and type of solid DAS was added. Agitation was provided as in Method A above. After 24 hr. the DAS had dissolved completely, and the pH values of the solutions were in the range of 7.1 to 7.7 for the different dialdehyde starches used.

Tanning at pH of about 10 was carried out in the same way as described above, except that 2.7% of magnesium oxide was used in addition to the 4.5% of sodium bicarbonate. The pH at the end of the 24-hr. tannage was in the range of 9.5 to 10.1.

The leather was then brought to a pH of about 4 as described in Method A. The shrinkage temperatures for the leathers immediately after tanning are shown in Table I under lots 1–12 (Method B) and for the acidified leathers under lots 13–24.

Fatliquoring.—The tanned specimens were fatliquored with a blend of 2 parts of sulfated neatsfoot oil and 1 part of 15° cold-test neatsfoot oil. Based on the wrung weight, 5% of oil and 100% of water were used, and fatliquoring was carried out at 55°C. At half-hour intervals two feeds of 1 ml. each of *5N* acetic acid were added to exhaust the fatliquor, the pH of the exhausted fatliquor being about 4.0.

Drying.—The tanned calfskin squares were first blotted between towels in a conditioned room maintained at 50% R.H. and 73°F. The towels were changed once or twice a day for 2 or 3 days or until the squares were apparently dry. Brass plates, heavy enough to prevent excessive curling, were kept on the squares during the drying period. When removed from the towels and plates, some of the poorly tanned specimens curled or warped excessively in the final stages of moisture adjustment. These were dampened slightly on the surface and put under sufficient weight so that they remained reasonably flat when dry again. The tanned leathers were allowed to reach moisture equilibrium in the conditioned room before testing.

Evaluation of experimental leathers.—The testing procedures were essentially the same as those described in a previous study (9); however, in the present test the comparisons were only between the various tannages and did not involve relations between the tanned and untanned skin.

Before the tanning, each conditioned, acetone-dehydrated square was weighed to 0.01 gram, its thickness was measured at five points and averaged, and the area of the combined 10 squares in each lot was measured with a planimeter. After the tanning, the conditioned leather squares were again measured as before, and yields were calculated.

Before test specimens were cut, the squares were examined by lots for general leather-like characteristics with the results summarized under "Leather Quality" in Table I.

After examining each lot as a whole, a grade for each lot was determined by mixing all 240 squares, then separating them into 5 piles on the basis of leather-like characteristics. Oiled specimens were, in general, much better than unoiled ones; however, in the grading an attempt was made to minimize the effect of oiling and to judge the pieces on thoroughness of tanning. Grade limits were established during sorting in order to avoid having an excessive number of squares in some grades. Grade 5 was best and Grade 1 poorest. The average grade for each lot is shown in Table I.

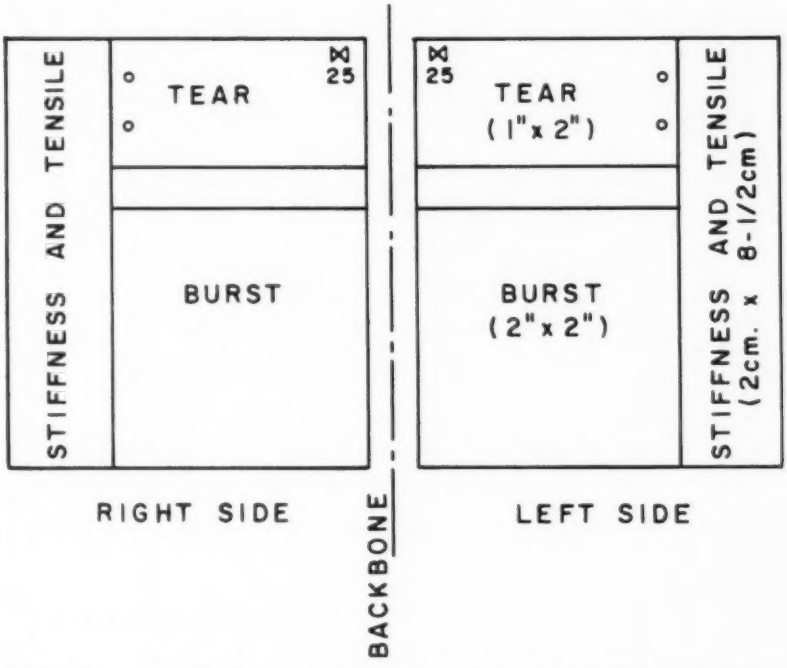

FIGURE 1.—Diagram of squares, from right and left sides, showing location of test specimens.

Test specimens were cut from each square according to the pattern shown in Fig. 1. Tensile, burst, and stitch tear strengths and elongation were determined by means of an Instron Tester, thus enabling calculations to be made of initial tear and energy of rupture as well. Elongation was calculated from plunger rise in the ball burst method as described by Clarke and Harris (10). Results of the physical and chemical tests are shown in Tables I and II for lots. The average values for each level of each main effect or tanning variable appear in Table III.

TABLE II

CHEMICAL AND PHYSICAL PROPERTIES OF DIALDEHYDE STARCH–TANNED CALFSKIN*

Lot or Tannage No.	Elongation at Rupture		Tear 2-hole Stitch Maximum		Tensile Strength		Burst Strength		Hide Substance	Fat	Water Solubles	Combined Tanni
	Tensile Method %	Burst Method %	Kg.	Kg/cm	Kg	Kg/cm²	Kg	Kg/cm	%	%	%	%
1	36	28	26	140	43	251	77	456	92.4	0.4†	2.3	4.7
2	32	30	25	131	38	206	74	404	87.7	.4†	3.0	8.7
3	36	33	17	81	36	173	71	346	92.2	.4†	1.5	5.6
4	36	37	17	86	28	136	65	307	93.0	.4†	1.6	4.9
5	26	30	23	103	32	150	63	295	90.8	.4†	2.3	6.4
6	25	31	20	86	32	151	63	286	90.4	.4†	2.5	6.5
7	41	36	21	94	29	132	66	329	94.0	.4†	1.5	3.8
8	40	37	21	85	31	138	70	324	91.3	.4†	1.6	6.4
9	39	34	20	81	32	138	64	264	92.9	.4	1.9	4.7
10	37	35	18	79	28	133	59	280	93.3	.3	1.6	4.7
11	39	40	23	85	36	138	69	272	94.6	.4	1.2	3.6
12	51	43	22	86	33	141	65	294	93.7	.3	1.2	4.6
13	36	34	24	118	39	181	63	305	86.6	7.7	1.9	3.5
14	29	32	26	139	33	176	63	356	87.3	7.9	2.0	2.5
15	57	45	26	126	40	207	68	372	83.8	9.1	1.6	5.2
16	48	47	28	122	43	193	70	338	83.2	9.4	1.6	5.3
17	48	35	27	121	40	174	70	317	85.2	8.6	2.2	3.7
18	43	39	24	113	40	184	64	311	83.0	8.6	2.3	5.8
19	52	47	28	122	50	245	76	383	86.0	8.4	1.3	3.9
20	59	46	27	130	45	210	75	376	83.5	8.6	1.6	5.9
21	65	54	29	114	44	186	69	305	83.3	8.3	2.2	5.8
22	53	49	28	115	47	187	73	292	86.8	7.6	1.5	3.8
23	76	58	30	118	49	202	75	301	85.4	8.2	1.7	4.2
24	71	60	33	131	48	196	83	333	87.7	7.7	1.6	2.4

*Ash (not shown) was difference between values shown and 100; values were usually between 0.1 and 0.3; highest value 0.6.
†Assumed values.

TABLE III

PHYSICAL TEST MEAN VALUES FOR DIALDEHYDE STARCH TANNAGES

Physical Property	Oxidation of Starch, %			Method of Dissolving Starch*		pH of Tannage		Fatliquor	
	33	67	95	a	b	8	10	Unoiled	Oiled
Grade	2.5	3.2	4.4	3.2	3.5	2.8	4.0	2.9	3.8
Area yield, %	95	98	92	94	96	94	96	93	97
Weight yield, %	115	117	114	115	115	116	115	111	120
Thickness yield, %	83	89	99	90	90	90	91	88	92
Stiffness, kg/cm²	1740	930	660	1190	1030	1550	670	1730	490
Elongation at grain crack, tensile, %	21	30	46	34	31	25	40	14	51
" " " ", burst, %	18	18	23	20	20	16	23	8	32
Load at grain crack, tensile, kg.	26	27	29	28	27	27	28	19	36
" " " ", burst, kg.,	32	30	30	31	30	29	32	18	44
Elongation at rupture, tensile, %	39	42	54	46	44	39	51	37	53
" " ", burst, %	36	38	47	40	41	36	44	35	46
Tear, 2 hole, initial, kg.	22	22	23	23	22	22	22	20	25
" ," ", " , kg/cm	106	98	92	99	99	102	96	88	110
" ," ", maximum, kg	24	24	25	25	24	24	25	21	28
" ," ", ", kg/cm " "	118	107	101	109	109	112	106	95	122
Tensile strength, kg.	37	37	39	39	37	37	39	33	43
" " , kg/cm²	190	173	165	181	171	176	176	157	195
Burst strength, kg.	69	68	70	69	69	67	71	67	71
" " , kg/cm	360	328	293	329	325	323	331	321	323
Energy of rupture, tensile, kg.	30	32	41	35	34	31	38	26	43
" " " , " , kgcm/cm²	150	148	173	161	153	143	171	120	194
" " " , burst, kgcm	21	21	23	22	21	21	22	21	22
" " " , " , kgcm/cm	110	98	95	102	100	101	101	98	104
Modulus of elasticity, kg/cm²	1460	680	280	890	720	1310	300	340	1270

* *a* = heating in autoclave; *b* = allowing to dissolve in buffered tan liquor.

After being tested, the specimens were combined by lots and ground for chemical analysis (9). The analytical data are shown in Table II.

RESULTS AND CONCLUSIONS

Statistical analyses.—The objective of these analyses was to determine the effect of a number of tanning variables on certain properties or characteristics of the leather. The variables and levels for each variable were constant from one property to another. There were in all 24 characteristics or properties; however, some of the tests presumably measured the same property.

The statistical design used in each of these 24 experiments is referred to as a factorial experiment. In each experiment the main four variables or main effects were as follows: oxidation or dialdehyde content of the starch, method of its solution, pH of tanning, and oil. As there are six combinations of four variables taken two at a time, we have six two-factor interactions. Similarly we have four three-factor interactions and one four-factor interaction. A significant interaction simply means that a combination of two or more of the four mentioned main effects or variables is more important than any single main effect for a particular property.

TABLE IV

ANALYSIS OF VARIANCE FOR GRADE

Source	Degrees of Freedom	Sum of Squares	Mean Square	F
Total	239	493	—	—
Replication	9	41	4.56	1.30
Oxidation (X)	2	138	69.00	19.71*
Solubility (S)	1	8	8.00	2.29
pH (P)	1	90	90.00	25.7*
Oiling (O)	1	49	49.00	14.0
XS	2	12	6.00	1.71
XP	2	26	13.00	3.71
XO	2	8	4.00	1.14
SP	1	1	1.00	.28
SO	1	1	1.00	.28
PO	1	3	3.00	.86
XSP	2	2	1.00	.28
XSO	2	1	.50	.14
XPO	2	6	3.00	.86
SPO	1	1	1.00	.28
XSPO	2	7	3.50	7.29†
Error	207	99	.48	

*Significant at the 5% level.
†Significant at the 1% level.

TABLE V

SIGNIFICANT F VALUES*

Test	Source of Variation† and Degrees of Freedom												
	X 2	S 1	P 1	O 1	XS 2	XP 2	XO 2	SO 1	PO 1	XSO 2	XOP 2	XSP 2	XSPO 2
Grade	20	—	26	—	—	—	—	—	—	—	—	—	7
Area yield													
Weight yield	—	—	—	71	—	—	—	—	—	—	8	—	—
Thickness yield	20	—	—	—	—	—	—	—	—	5	—	7	—
Stiffness	—	—	—	—	3	—	—	—	—	—	26	—	—
Stretch at grain crack, tensile	19	—	—	63	3	—	—	—	—	—	3	—	—
Stretch at grain crack, burst	—	—	—	54	—	—	13	—	15	—	—	—	—
Load at grain crack, tensile, kg.	—	—	—	46	—	—	—	—	—	—	—	—	6
Load at grain crack, burst, kg.	—	—	—	36	—	—	—	—	10	5	—	—	—
Elongation at rupture, tensile	—	—	—	—	—	—	—	—	—	—	4	—	—
Elongation at rupture, burst	—	—	—	—	—	—	11	—	4	—	—	—	—
Tear, 2 hole, initial kg.	—	—	—	—	—	—	—	4	—	—	11	—	—
Tear, 2 hole, initial kg/cm	—	—	—	—	—	—	—	9	—	—	16	—	—
Tear, 2 hole, maximum kg.	—	—	—	—	—	—	—	—	—	—	7	—	—
Tear, 2 hole, maximum kg/cm	—	—	—	47	—	—	—	—	—	—	—	—	3
Tensile strength kg.	—	4	—	20	—	—	—	—	—	—	5	—	—
Tensile strength kg/cm²	—	—	—	—	3	—	—	—	—	—	10	—	—
Burst strength kg.	—	—	—	—	—	—	10	—	4	—	—	—	—
Burst strength kg/cm	—	—	—	—	—	—	—	—	—	—	—	—	3
Energy of rupture, tensile kgcm	—	—	—	22	—	—	—	—	—	—	7	—	—
Energy of rupture, tensile kgcm/cm²	—	—	—	20	—	—	—	—	—	—	7	—	—
Energy of rupture, burst kgcm	—	—	—	—	—	5	15	—	5	—	—	—	—
Energy of rupture, burst kgcm/cm	—	—	—	—	—	—	—	—	—	—	12	—	—
Modulus	—	—	—	—	—	—	—	—	—	4	25	—	—

*All values rounded to whole numbers. Critical values of F for an error term with 207 degrees of freedom and greater mean squares with degrees of freedom of 1, 2, and 9 respectively are as follows: 5% point 3.9, 3.0, and 1.9; 1% point 6.8, 4.7, and 2.5; 0.1% point 11.3, 7.2, and 3.4; dash (—) indicates nonsignificant value of F.

†Letters have the following significance: X = degree of oxidation of starch; S = method of dissolving starch; P = pH of tan liquor; O = oiling method; XS, XP, etc. = interactions. Two interactions, SP and SPO, are not shown, since none of the F values were significant.

Table IV is the analysis of variance table for grade of leather and illustrates how the data were handled. A similar table was computed for all the other properties but is not included here for sake of brevity. The complete analysis of variance tables will be published elsewhere. Areas were determined by lots and not on individual squares, so an analysis of variance was not made. From the analysis of variance tables the F values that were significant at the 5% level or less were obtained, and these are summarized in Table V.

Best tanning conditions for dialdehyde starch.—From the analysis of variance tables and from the significant F values (Table V) the best tanning conditions, as shown by the various tests, were selected and are indicated in Table VI. The optimum tanning factors were considered to be those

TABLE VI

BEST* TANNING CONDITIONS AS SHOWN BY VARIOUS TESTS

Test	DAS Oxidation %	DAS Method of Solution†	pH of Tanning	Oil‡
Grade	96	—**	10	+
Area yield††	67	b	10	+
Weight yield	67 (33)	—	8 (10)	+
Thickness yield	96	b	10	+
Stiffness	96	b	10	+
Elongation at grain crack, tensile	96	a	10	+
Elongation at grain crack, burst	96	—	10	+
Load at grain crack, tensile	96	—	—	+
Load at grain crack, burst	96 (67)	—	10	+
Elongation at rupture, tensile	96	—	10	+
Elongation at rupture, burst	96	—	10	+
Tear, 2 hole, initial, kg.	96 (67)	—	—	+
Tear, 2 hold, initial, kg/cm	33	a	8	—
Tear, 2 hole, maximum, kg.	96	—	10	+
Tear, 2 hole, maximum, kg/cm	33	—	8	—
Tensile strength, kg.	96	a	10	+
Tensile strength, kg/cm^2	33	a	8	—
Burst strength, kg.	96	—	10	+
Burst strength, kg/cm	33	a	8	—
Energy of rupture, tensile, kgcm	96	—	10	+
Energy of rupture, tensile, kgcm/cm^2	96	—	10	+
Energy of rupture, burst, kgcm	96	—	10	+
Energy of rupture, burst, kgcm/cm	33	—	8	—
Modulus of elasticity, kg/cm^2	96	—	10	+

*Best values were considered to be high values for all tests except stiffness and modulus, for which low values were best.
†*a* denotes dissolving DAS by autoclaving; *b* denotes allowing the solid DAS to dissolve in the buffered tan liquor.
‡ + indicates presence of oil and — absence of oil.
** — denotes that factor was not significant.
††From data in Tables I and III (not treated statistically).

that gave the highest values for all the properties or tests, except stiffness and modulus. It should be borne in mind that the optimum or best conditions which result from these analyses are not necessarily the true optimum conditions. That is, these optimum conditions are only optimum for the four different variables and the levels of each used in these experiments. For example, in general, the condition with oil was greatly superior to that with no oil, although in each of these 24 analyses only one type of oil was used and only one amount of this particular type of oil. Therefore, no inference can be made about all types of oil or different amounts of oil. In addition, the raw stock used for this study was acetone-dehydrated; however, the influence of this factor was not evaluated.

Inspection of Table VI clearly shows that the best properties resulted from particular combinations of usually more than two tanning variables. In most cases the manner of dissolving the dialdehyde starch did not appear to be significant; thus this factor can be safely ignored because of its slight influence on leather properties. This conclusion was based on a constant time factor of 24 hours for the tannage, which permits sufficient time for solution of the DAS by Method B and tanning by the dissolved material. It has been noted that several hours were required for solid DAS to dissolve at room temperature in the tanning liquor at pH about 8. Hence in tanning for short periods of time the rate of solution of the solid DAS (Method B) may become the dominant factor. Solution of the material beforehand, either by autoclaving or by warming with alkaline agents (borax, bicarbonate, etc.), would be preferred for a rapid tannage with dialdehyde starch.

The use of Table VI is best illustrated by an example. Thus in the case of thickness yield the thickest leather resulted when dialdehyde starch of 96% oxidation was used at pH 10, allowing the solid to dissolve in the alkaline tan liquor, and oiling of the leather. Although not shown in the table, the flattest or thinnest leather came from tanning with 33%, oxidized dialdehyde starch, at pH 8, without oiling. This explains why the strength properties on a unit thickness or area basis were highest for the leathers made with this combination of tanning variables. Since the 33% oxidation level dialdehyde starch in general produced the poorest quality leather (except tannage No. 16 in Table I), it can be eliminated as a satisfactory agent for tanning. With but few exceptions all the other properties were at a maximum when dialdehyde starch of 96% oxidation (DAS-96) was used at pH 10, with oiling. This particular combination of tanning factors, i.e., DAS-96, pH 10, and oil, was found to give the optimum with respect to the following characteristics: grade of leather, thickness yield or plumpness, flexibility, grain crackiness, stretch, tear strength, breaking load (tensile), burst strength, and energy of rupture. In two cases, load at grain crack (burst) and initial tear (kg), both the 96% and the 67% oxidation levels produced optimum values. The area yield was highest for the tannage with DAS-67 added as the solid to the

tanning liquor at pH 10, and oiled. The best weight yield was noted under two sets of conditions. One was tannage with DAS-67 at pH 8 after oiling, and the other with DAS-33 at pH 10 after oiling.

It is noted in Table VI that there is a high degree of correlation between the tensile and burst methods for measuring the strength, elongation, and energy of rupture of the leather.

SUMMARY

Pickled calfskins were dehydrated with acetone and cut into 3¼" squares. These were combined randomly into lots of 10 squares each. A lot was then assigned at random to each of 24 tannages. The tanning variables included: (*a*) dialdehyde starch of three oxidation levels, namely 33, 67, and 96%; (*b*) two procedures for dissolving the dialdehyde starch; (*c*) tanning at two pH levels, namely 8 and 10; and (*d*) oiled and unoiled condition. After being tanned, the leathers in each lot were dried and evaluated. The data were treated statistically. In general the procedure for dissolving the dialdehyde starch did not appear to be significant in a 24-hr. tannage. The dialdehyde starch oxidized to the 33% level produced the flattest leather, which was of poor quality. Maximum leather quality was obtained with dialdehyde starch of the highest oxidation level, i.e., 96%. Tanning with DAS-96 (dialdehyde starch oxidized to the 96% level) at pH 10 and oiling the leather was optimum with respect to the following leather characteristics: grade, thickness yield, flexibility, grain crackiness, stretch, tear strength, breaking load (tensile), burst strength, and energy of rupture. Area yield was highest for tannage with DAS-67, added as the solid to the tanning liquor, at pH 10 and oiling of the leather. Optimum weight yield was noted in tannages with DAS-67 at pH 8 or DAS-33 at pH 10 after oiling.

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SOLVENT EXTRACTION

REPORT OF THE ALCA VEGETABLE LEATHER SUBCOMMITTEE

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With the assistance of

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INTRODUCTION

In June, 1955, the use of chloroform as a solvent for oils and greases in vegetable leather was discussed at a meeting of the ALCA Vegetable Leather Committee. A number of leather chemists had questioned the use of chloroform, contending that it gave misleading and incorrect results for oil and grease in vegetable leather, particularly sole leather. A subcommittee consisting of I. D. Clarke, H. R. Miller, A. N. Kay, and C. A. Blair was appointed to study the effect of using the Soxhlet extractor and the ASTM extractor. These extractors were permitted in Method B4.

Two samples of leather were sent to the committee—one sole leather (Sample 1) and one upper leather (Sample 2). The results of the work are given in Table I.

TABLE I

	Sample 1		Sample 2	
	Soxhlet %	ASTM %	Soxhlet %	ASTM %
I. D. Clarke	4.64	4.33	9.13	9.02
A. N. Kay	4.76	4.68	10.18	8.65
H. R. Miller	4.18	4.42	9.20	9.05
C. A. Blair	4.88	4.31	9.19	9.25

The result of this work was the recommendation that a provisional method be adopted for solvent extract, using the Soxhlet extractor and petroleum ether (B.P. 50° C.-80° C.) as solvent for vegetable-tanned rough welting, sole leather, and rough belting leather. For other types of vegetable leather U. S. P. chloroform was to be used (Provisional Method B4, June, 1957).

On June 17, 1956, the Vegetable Leather Committee instructed the subcommittee to investigate other solvents, evaporation loss of oiling constitu-

ents which may affect moisture determination, and solvent extraction and drying time. As these instructions were very broad, it was decided to investigate other solvents first. Dr. Lollar assisted the committee by conducting some preliminary work. While using ligroine, hexane, chloroform, and carbon tetrachloride he found that all of these solvents extracted a material with a higher saponification value than the oil used. The chloroform extract had a much higher saponification value than any other solvent. The results of his work, which are shown in Table II, indicate that chloroform is not the proper solvent for sole leather.

TABLE II

PERCENT SOLVENT EXTRACTABLE PORTION IN LEATHER COMPONENTS

Solvent	Tanning Liquor Blend	Epsom Salts	Corn Sugar	Oil	Filler		Leather Sap. Value of Extract
Petroleum ether, B.P. 30°–60° C.	0.0	Trace	0.73	98.5	0.12	4.76	88
						4.67	92
Ligroine	0.0	0.0	1.34	99.4	0.11	4.88	83
						5.00	87
Hexane, B.P. 65°–67°C.	0.0	0.0	0.15	98.9	0.03	4.85	87
						4.95	107
Chloroform, reagent	0.0	0.0	0.28	100.0	1.72	5.51	130
						5.43	130
Chloroform, anhydrous	0.0	0.0	0.45	100.0	2.10	5.45	150
						5.45	143
Carbon tetrachloride, reagent	0.0	0.0	0.00	100.0	0.10	4.77	88
						4.97	96

Tanning-liquor blend dispersed on cotton before extraction; extract weight corrected for extracts in cotton.
Epsom salts and filler extracted in Soxhlet extractor, using 5-g. portions.
Corn sugar and oil extracted in liquid—liquid extractor.
Saponification value: oil, 52; filler, 209.

On the basis of the preliminary work, it was decided to make comparative extractions using:

1. Petroleum ether Fisher E-139 B.P.—30°-60° C.
2. Hexane Fisher H-291 B.P.—65°-67° C.
3. Chloroform A.C.S. B.P. 58°-61.5° C.
4. Carbontetrachloride A.C.S. B.P. 76.8° C.

STATISTICAL EXAMINATION OF THE DATA

The data secured are shown in Table III.

The experimental plan under which the work of the subcommittee was conducted was designed to provide that

(*a*) An unbiased estimate could be made of the results secured to determine the effect of the four selected solvents upon the amount of solvent extractive in each leather.

(*b*) An unbiased estimate could be made of the results secured to determine the within-day, the between-day, and the between-laboratory contribution to the precision or reproducibility of the results secured.

TABLE III

DATA ON SOLVENT EXTRACTION OF LEATHER

Lab.	Leather 1		Leather 2		Leather 3		Leather 4	
	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2	Day 1	Day 2
				Solvent: Petroleum Ether				
1	4.27	4.22	3.77	3.78	17.68	17.68	9.44	9.59
	4.37	4.17	3.74	3.64	17.68	17.58	9.54	9.59
2	4.19	4.01	3.51	3.52	17.51	17.55	9.20	9.24
3	4.14	4.22	3.75	3.49	17.60	17.76	9.36	9.38
	4.14	4.27	3.75	3.58	17.62	17.80	9.30	9.49
4	3.75	3.71	3.46	3.63	17.42	17.07	9.82	9.35
	3.92	3.54	3.51	3.54	17.52	17.07	9.71	9.25
				Solvent: N-Hexane				
1	4.45	4.13	3.68	3.66	18.03	17.79	10.17	10.28
	4.42	4.23	3.67	3.64	18.11	18.03	10.05	10.36
2	4.07	4.11	3.94	3.98	17.93	17.90	10.40	10.38
3	4.04	4.13	3.80	3.67	17.99	17.96	9.74	10.24
	4.11	4.17	3.80	3.66	18.08	18.09	9.96	9.81
4	3.88	3.81	3.90	3.52	17.57	17.32	10.61	10.40
	3.86	3.84	3.79	3.50	17.49	17.19	10.62	10.24
				Solvent: Chloroform				
1	4.57	4.28	4.04	3.95	19.10	18.96	12.57	12.78
	4.57	4.50	4.10	3.91	19.07	18.86	12.61	12.69
2	4.37	4.40	4.36	4.33	18.96	18.99	12.62	12.63
3	4.55	4.56	3.92	4.04	18.93	18.80	12.42	12.35
	4.58	4.56	3.89	4.08	18.98	18.95	12.40	12.24
4	4.05	4.14	4.33	3.80	18.47	18.41	12.98	12.79
	4.03	4.02	4.25	3.75	18.49	18.33	12.88	12.68
				Solvent: Carbon Tetrachloride				
1	4.45	4.31	3.81	4.10	18.41	18.13	11.24	11.31
	4.42	4.35	3.59	3.81	18.24	18.32	11.21	11.41
2	4.25	4.21	3.68	3.71	18.34	18.30	11.16	11.13
3	4.24	4.26	4.03	4.12	18.20	18.41	11.14	10.80
	4.27	4.28	3.44	3.83	18.12	18.51	10.93	11.15
4	4.02	4.23	3.84	3.78	18.19	17.81	11.78	11.26
	4.10	4.05	4.02	3.81	18.12	17.68	11.82	11.31

The experimental plan did not contemplate any statistical comparison of the content of solvent extractives in the four different leathers. The same experimental plan was applied separately to each of four leathers selected by the subcommittee to be typical of leathers which might be analyzed by the solvent extraction procedure.

The solvents used, petroleum ether, n-hexane, chloroform, and carbon tetrachloride, were selected as specific solvents on the basis of previous work; no attempt was to be made to generalize from the data secured with respect to the ability of other solvents to extract materials from leather. The laboratories selected to participate in the work were regarded as a random sample of the larger group of laboratories that might use the method; the original experimental plan provided for four individual laboratories. Since one laboratory did not complete the experimental plan, the statistical examination of the data is based upon the work of three laboratories.

The applicable analysis of variance for the experimental plan therefore is:

Source of Variance	Degrees of Freedom	Components of Variance
Between solvents	4–1 = 3	$\sigma\text{-}_r^2 + 2\sigma\text{-}_{se}^2 + 6\sigma\text{-}_s^2$
Between laboratories	3–1 = 2	$\sigma\text{-}_r^2 + 8\sigma_e^2$
Interaction: solvent by laboratories	3 × 2 = 6	$\sigma\text{-}_r^2 + 2\sigma\text{-}_{se}^2$
Daywise replication	4 × 3(2–1) = 12	$\sigma\text{-}_r^2$
Within-day duplication	4 × 3 × 2(2–1) = 24	
Total	4 × 3 × 2 × 2 –1 = 47	

This experimental plan provided that the within-day duplication source of variance provide only the desired information on the magnitude of this source of error. The proper error term for the main portion of the experiment is shown by the components of variance indicated above. It will be noted the solvent contribution to variance is estimated against the interaction as an error term, while the laboratory source of variance is estimated against the daywise replication as an error term.

Table IV presents the statistical data which were secured from the experimental work by the subcommittee. Based upon the data in this table, the following conclusions may be drawn from the data secured by the committee:

(*a*) The four solvents have given dissimilar results on each of the four leathers, unless a chance occurrence which is very improbable has in fact occurred in these experiments.

(*b*) The three laboratories have given dissimilar results on three of the four leathers, unless a chance occurrence which is very improbable has in fact occurred in these experiments.

TABLE IV

STATISTICAL ANALYSIS OF DATA ON SOLVENT EXTRACTION OF LEATHER

Source of Variance	Degrees of Freedom	Leather 1 Mean Square	Leather 1 F-Value	Leather 2 Mean Square	Leather 2 F-Value	Leather 3 Mean Square	Leather 3 F-Value	Leather 4 Mean Square	Leather 4 F-Value
Between solvents	$4-1=3$	0.2479	7.36	0.3315	22.40	3.4644	154.66	22.2397	631.81
Between laboratories	$3-1=2$	0.8139	50.24	0.0041	Insig.	1.2038	23.70	0.7348	11.93
Solvent × laboratories	$3\times2=6$	0.0337	Insig.	0.0148	Insig.	0.0224	Insig.	0.0352	Insig.
Daywise replication	$4\times3(2-1)=12$	0.0162	—	0.0532	—	0.0508	—	0.0616	—
			3.93		3.83		8.71		5.48
Within-day duplication	$4\times3\times2(2-1)=24$	0.00412		0.01390		0.00583		0.01124	

Tabular Percentage Points of F-Ratio

Source of Variance	Degrees of Freedom	10%	5%	1%	0.5%
Solvent	3/6	3.29	4.76	9.78	12.92
Laboratories	2/12	2.81	3.89	6.93	8.51
Replication	12/24	1.83	2.18	3.03	3.41

Component of Variance	Leather 1	Leather 2	Leather 3	Leather 4
Solvent	0.0357	0.0528	0.5737	3.7008
Laboratories	0.0997	Insig.	0.1441	0.0842

(*c*) The statistical interaction is not significant on any of the four leathers; the four solvents did not give dissimilar results in the hands of the three laboratories.

(*d*) The laboratory between-day replication results are not as consistent as the within-day duplication estimate of variance would suggest, unless a chance occurrence which is very improbable has in fact occurred.

(*e*) All probability statements inherent in the above four conclusions are based upon the usual assumption that the critical F-ratio is the 5% level; to assist the reader, the data of Table IV present the appropriate tabular data for F-ratios taken from standard statistical tables.

(*f*) Examination of the components of variance and the data secured suggests:

1. Petroleum ether and n-hexane give rather consistent results; this is of course logical, since the n-hexane is but a closer boiling fraction of the petroleum ether type of solvent.
2. The two chlorinated solvents have given higher levels of solvent extractives, with chloroform giving the highest level on all four leathers.
3. The precision of the method will leave much to be desired unless further committee work is done to ascertain the causes of the significant defect due to laboratories on three of the leathers, and the significant daywise effect on all leathers for all solvents.
4. There is the possibility that examination of the procedures employed by laboratory 4 in comparison with those employed by laboratories 1 and 3 might assist in the development of the necessary committee work indicated in item 3. Laboratories 1 and 3 were very close on leathers 1, 2, and 3, while laboratory 4 secured lower results on these leathers. No conclusions on interlaboratory concordance can be drawn for leather 4.

(*g*) While the data from laboratory 2 could not be included in the statistical examination, since this laboratory did not complete the experiment, it should be noted that the available data from laboratory 2 would fit into these same conclusions. With respect to the laboratory contribution to variability, laboratory 2 is similar to laboratory 1 and laboratory 3 on leathers 1, 3, and 4; on leather 2, laboratory 2 would find higher solvent extractives than the other three laboratories.

CONCLUSIONS

The significance of the work conducted by the committee may be illustrated by consideration of the fact that one would expect two thirds of all values to

lie within plus or minus one standard deviation range from a true average or central tendency of normally distributed data. The components of variance for solvent and for laboratory given on the lower part of Table IV may be used to estimate the contribution of the solvent and the laboratory to the dispersion of analytical results, using the standard deviation as the dispersion estimate.

The largest variance component for solvent, that secured on leather 4, is 3.7008; this is equivalent to a standard deviation of 1.92% extractive. The largest variance component for laboratory is 0.1441; this is equivalent to a standard deviation of 0.38% extractive.

It seems to the Committee that it would be best to accept n-hexane as the solvent of choice. Then, the laboratory method could be studied in an attempt to lower the contribution of the laboratory to the variability of the results.

APPENDIX

COMMENTS ON STUDY OF SOLVENT EXTRACTION OF VEGETABLE LEATHER

The following supplementary statistical analysis of the experimental results (Table III) was made by Mr. John Mandel, National Bureau of Standards, according to the statistical model suggested by him for use in interlaboratory evaluation of test methods (ASTM Bulletin, July, 1959, page 53).

The data were analyzed in two ways.

In the first approach all methods (solvents) were included in a single, over-all analysis. The model involved 16 sets of data (4 laboratories × 4 methods) for each of 4 materials. For each material the average of all 16 sets was computed. The data for each set were then plotted versus those averages. The central point, μ, of the fitted line, its slope, β, and the scatter about the line, V (η), are tabulated in Table A for all 16 sets, classified according to method and laboratory. The CCl_4 method stands out in two ways: small V (η) and small variation among laboratories, both in μ and in β.

TABLE A

STATISTICAL ANALYSIS OF DATA

	μ				β				V (η)			
Lab.	P.E.	N.H.	Chl.	CCl_4	P.E.	N.H.	Chl.	CCl_4	P.E.	N.H.	Chl.	CCl_4
1	8.80	9.05	10.04	9.44	.956	.987	1.062	1.009	.497	.151	.581	.037
2	8.59	9.09	10.08	9.35	.958	.980	1.049	1.021	.656	.082	.531	.015
3	8.73	8.95	9.95	9.36	.962	.990	1.050	1.011	.627	.295	.348	.0002
4	8.52	8.85	9.84	9.36	.958	.967	1.041	1.000	.230	.011	1.245	.221

In view of the small number of materials included in the experiment, the significance of these results is questionable. To obtain further information, a second analysis was made.

TABLE B

STATISTICAL ANALYSIS OF DATA

Source of Variation	D.F.	M S			
		P.E.	N.H.	Chl.	CCl_4
Laboratories	3	.0645	.0470	.0460	.0079
Laboratories × materials	9	.0203	.0514	.0482	.0313
Slopes	6	.0018	.0168	.0075	.0095
V (η)	3	.0295	.0688	.0686	.0422

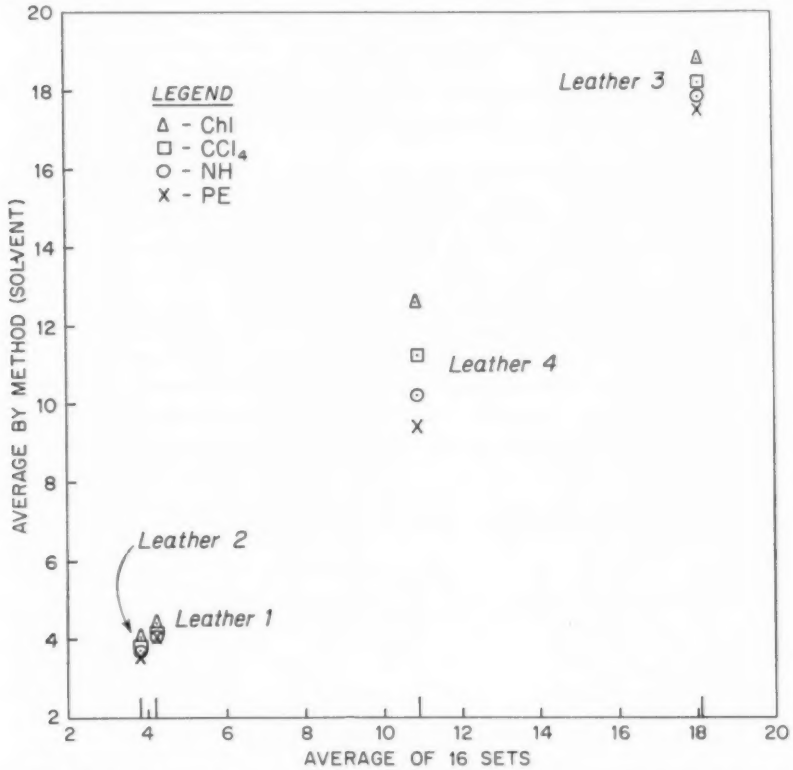

FIGURE 1.—Percent grease. Average values by method vs. average value for each leather.

In the second approach, separate analyses were made for the 4 mtehods. Table B shows the analyses of variance, in which the laboratories × materials interaction is broken down into two parts: systematic differences in the slopes (β) of the laboratories, and random scatter about the individual response lines for each laboratory, V (η). This analysis fails to show the differences in V (η) observed in the first analysis. The reason for this can be seen by examining Fig. 1. The leather with about 10% solvent-extractive (leather 4) shows considerable scatter among the four solvents. The results for CCl_4 for this leather are, however, intermediate between those obtained by the other three solvents. Therefore, the CCl_4 points show less scatter with regard to the over-all solvent averages than the points corresponding to the other solvents.

It is not possible to decide, on the basis of these data, whether this apparent better behavior of the CCl_4 data is real or accidental. Table B shows a considerably smaller mean square for laboratories than the other solvents. On the other hand, even for these other solvents, the laboratory effect is not significant with respect to the random scatter V (η). It is possible that leather 4 contains substances that interfere with the analysis by all solvents except CCl_4, but such a possibility is only speculation at this point.

There appears to be a need for further work, based on a much larger number of leathers, to establish with reasonable certainty the relationship among the 4 solvents.

As difficult as it sometimes is to draw the distinction in actual practice, science and engineering are clearly not the same thing. Science aims at the discovery, verification, and organization of fact and information. Its goal is an understanding of the world we live in and of ourselves as part of that world. It seeks truth and knowledge. The scientist puts nature under his microscope to discover how it behaves and why it behaves that way. Having done this, he seeks to order the facts he discovers into general, or "universal," laws through induction and hypothesis—laws that can stand as an accurate, quantitative description of the organization and operation of nature.

We get "science" from the Old French word meaning "to know"; "engineering" derives from the Old French word meaning "to produce." To an engineer, knowledge is not an end in itself but is simply the raw material from which he fashions structures, machines, and processes. He directs his attention primarily not to the discovery of facts and information but to their application and utilization. His task is to take the knowledge acquired through the study of an existing system—that is, nature—and use it to design a new system to serve a human purpose. If science is basically analytical, engineering is basically creative. If the characteristic method of the scientist is induction, then that of the engineer is deduction. If understanding is the basic goal of the scientist, then utilization is the basic goal of the engineer.

—Eric A. Walker. "Engineers and/or Scientists." *Journal of Engineering Education*. Vol. 51, No. 5, Feb. 1, 1961. Reprinted by permission of the American Society for Engineering Education.

ZIRCONIUM DETERMINATION BY GRAVIMETRIC METHODS*

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ABSTRACT

This work was stimulated by interest in the determination of zirconium by the Mineral Leathers Committee of the American Leather Chemists Association. Following a review of some known gravimetric methods, an investigation was made of one recently reported using Tartrazine. Under the conditions described, direct weighing was not possible, some occlusion of titanium occurred at the preferred acidity, and complete precipitation did not take place in strongly acidic solutions, even though these were free from sulfates. However, by suitable adjustment of the acidity and ignition of the washed precipitate at a high enough temperature, good results were obtained. These compared favorably with those found by other recognized methods. Hence Tartrazine can be utilized to advantage in the analysis of leathers containing zirconium.

INTRODUCTION

Early in 1959 the Mineral Leathers Committee decided to consider methods for analysis of zirconium in leather. At the Annual Meeting at Mackinac in June a program for immediate action was drawn up, the first step being to run independent determinations of zirconium and titanium in solutions containing only these heavy metals in known concentrations. The method to be followed was that suggested by the present authors in 1953 (1), i.e., precipitation of zirconium and titanium together by means of p-hydroxyphenyl arsonic acid, ignition to combined oxides, determination of TiO_2 colorimetrically in another aliquot of the analytical solution, and calculation of ZrO_2 by difference. We agreed to prepare the reference solutions for distribution to the committee members. After overcoming some unexpected difficulties we obtained four stable solutions, A, B, C, and X, containing

*Presented by Dr. I. C. Somerville at the ALCA Annual Meeting at Lake Placid, June 21, 1960.

different ratios of these metals. We found it necessary to eliminate sulfates by ashing and carbonate fusion in order to secure accurate results in the colorimetric determination of TiO_2. This would not be achieved when using a wet oxidation, suggested as an alternative method for preparing an analytical solution from leather.

Reference solutions A, B, and C were sampled to those interested. The results will be reported in detail elsewhere, but it can be stated here that good agreement was obtained for both ZrO_2 and TiO_2.

REVIEW OF KNOWN GRAVIMETRIC METHODS

While this analytical work was in progress we decided that it might be of interest to make a general review of the gravimetric methods available for the determination of zirconium, some of which are widely utilized in industrial practice today. When only zirconium salts are present in the solution, the simplest method is to precipitate with ammonia, wash thoroughly, dry, and ignite to ZrO_2. Many pioneer investigations were concerned with prior separation of other metals which would also precipitate along with zirconium when using ammonia or even more selective reagents. It was necessary to differentiate from impurities such as iron, titanium, aluminum, vanadium, thorium, and the rare earths, particularly when analyzing for zirconium in mineral ores. The classical methods for gravimetric determination were summarized by Furman in 1939 in Scott's *Standard Methods of Chemical Analysis* (2). The reagents used were cupferron (ammonium salt of nitrosophenylhydroxylamine), selenious acid, ammonium phosphate, and phenylarsonic acid. Reference is made to the presence of hafnium in small amounts in all naturally occurring minerals containing zirconium, and this is precipitated along with zirconium by all these reagents, but the residue on ignition is calculated as if only zirconium oxide is present. Brief comments on these methods are given below.

The use of cupferron requires a double precipitation, first with ammonia to remove alkali salts, then with the reagent. Iron has to be previously removed from the solution. The precipitate also contains titanium and any rare earths present, which must be determined separately and deducted from the total residue after ignition, giving ZrO_2 by difference.

The solution for selenious acid precipitation must be free from phosphate and sulfate. This method also requires a double precipitation, first adding the reagent directly, then repeating after the precipitate has been taken up in hydrochloric acid and the solution treated with hydrogen peroxide to keep the titanium in solution. The washed precipitate is ignited directly to ZrO_2.

The solution for precipitation with ammonium phosphate is made strongly acidic (3.6*N*) with sulfuric acid and is also treated with hydrogen peroxide.

The washed precipitate is ignited carefully to ZrP_2O_7, and a factor is used to convert to ZrO_2. The presence of Hf introduces some uncertainty as to the exact factor which should be used in this calculation.

Phenyl arsonic acid is more selective than some of the other reagents tried, but the solution must be acidified with hydrochloric acid and also treated with hydrogen peroxide to keep the titanium in solution. Simple ignition of the precipitate "gives results which are a little high, due to retention of arsenic, but if the ignition is finished over the blast in a current of hydrogen the results are correct."

In addition to these standard methods many other reagents for the precipitation of zirconium have been described in the literature. In our experience one of the most useful has been p-hydroxyphenyl arsonic acid, described in 1938 by Simpson and Chandlee (3). This method was first developed with the object of securing a selective reagent for titanium, but it was found to be excellent also for zirconium. These metals were separated by adding hydrogen peroxide to the solution before adding the reagent, as utilized in some of the above methods. The use of mandelic acid (phenylglycolic acid) was first suggested in 1947 by Kumins (4), and this has been found to be a good selective reagent for zirconium by many analysts, for example, Hahn (5), and Hill and Miles (6). Since precipitation is not complete in the presence of more than a small amount of sulfates, in some cases a double precipitation is required, first with ammonia, then with the reagent. An improvement over the use of mandelic acid was effected by utilizing substituted mandelic acids, which give precipitates of greater bulk for the same amount of zirconium, but which are more expensive. A series of glycolic acid derivatives of this type were investigated in 1949 by Oesper and Klingenberg (7). They selected p-bromo- and p-chloromandelic acid, in this order of preference, over mandelic acid alone. The precipitate obtained with the latter consists of zirconium tetramandelate, but this is appreciably soluble in water so that washing must be carried out with a hot solution of 2% hydrochloric acid plus 5% mandelic acid, making it impossible to weigh the precipitate directly before ignition. The corresponding tetrahalomandelates can be washed with water without loss of zirconium. Hence they found it possible to weigh these directly when precipitated from pure zirconyl chloride solutions although not from solutions prepared from alloy and ore samples. This procedure was utilized in 1951 by Hahn (8) to determine zirconium-hafnium ratios in pure solutions of the oxychlorides. Under properly controlled conditions he obtained precipitates corresponding to the theoretical composition, $Zr(C_8H_6O_3Br)_4$ and $Hf(C_8H_6O_3Br)_4$. These were dried at 120°–130°C., weighed, ignited to the oxide, and weighed again. From these data the hafnium content of any mixture could be calculated. Precipitates of theoretical composition were obtained only in hot solutions about 2*N* in hydrochloric acid and using a two- to three-fold excess of p-bromomandelic acid. The

presence of a certain amount of free sulfuric acid aided in obtaining precipitates of constant composition. The time for complete analysis was only one-fourth of that required for spectrographic analysis by the selenite method, and the results compared favorably with the latter. In 1955 Papucci and Klingenberg (9) confirmed the merits of p-bromo- and p-chloromandelic acids for determining zirconium in magnesium alloys. They secured much faster results than by the phosphate method, and these were the same as those found by the colorimetric method using Alizarin Red S.

Most of these methods were developed for recovery of zirconium from minerals containing other inorganic metals or in connection with the determination of metallic zirconium in various alloys. In the field of leather and tanning materials the problem is usually a simpler one, even though a considerable number of elements may be present in, for example, finished white leather tanned with zirconium. An exploratory scheme for quantitative examination of a system of this type was described in June, 1952, by the present authors (10). This was based primarily on separation of individual metals following the carbonate fusion and on precipitation of appropriate solutions with ammonia or p-hydroxyphenyl arsonic acid. Later in the same year a review was made in France by Grach (11), who listed nine possible methods of zirconium analysis and selected those based on ammonium phosphate or mandelic acid.

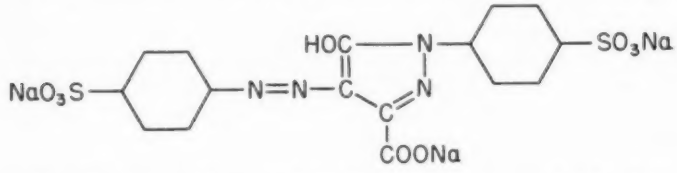
Within the last year or so a number of new gravimetric methods have been suggested, including the use of Tartrazine by Baiulescu and Turcu (12), of thiodiglycolic acid (13) and of thiomalic acid (14) by Sant and Sant, and of precipitation with p-chloromandelic acid followed by determination of zirconium as the alizarin lake by Evans, Hrobar, and Patterson (15). We were intrigued by the proposed use of Tartrazine, as it was claimed that it could be used to precipitate zirconium selectively in presence of titanium and that the precipitate could be dried and weighed directly without requiring ignition. We decided to apply this method to the determination of zirconium in tanning solutions, and this investigation constitutes most of the original work reported in this paper.

Since this paper was presented, a comprehensive review of "The Analytical Chemistry of Zirconium" by G. W. C. Milner and J. W. Edwards (16) came to our attention. In addition, a paper on "The Determination of Zirconium with Benzoylphenylhydroxylamine" by D. E. Ryan (17) has since been published. In both cases reference is made to the Tartrazine method selected for further study in this investigation.

PRECIPITATION OF ZIRCONIUM WITH TARTRAZINE

The method described by Baiulescu and Turcu in Bucharest, Roumania, (12) was suggested by observations on the precipitating action of certain types of mono-azo dyestuffs for zirconium and hafnium. They reported that

a 2% aqueous solution of Tartrazine gave an immediate precipitate with a solution of zirconium nitrate or oxychloride in an acidic solution at pH 1 or



lower. On filtering, washing, and igniting, consistent results for ZrO_2 were obtained, reproduced in Table I.

TABLE I

TARTRAZINE METHOD BY BAIULESCU AND TURCU

Volume of $ZrOCl_2$ solution ml.	Zr Calculated g.	Zr Found g.	Zr Difference mg.
5	0.0050	0.0050	± 0
10	0.0100	0.0099	− 0.1
10	0.0100	0.0100	± 0
10	0.0100	0.0100	± 0
12.5	0.0125	0.0126	+ 0.1
12.5	0.0125	0.0125	± 0
15	0.0150	0.0150	± 0
20	0.0200	0.0200	± 0
25	0.0250	0.0249	− 0.1
30	0.0300	0.0298	− 0.2

Anal. Chim. Acta, 21, 34 (1959).

TABLE II

DIRECT WEIGHING METHOD OF BAIULESCU AND TURCU

Volume of $ZrO(NO_3)_2$ solution ml.	Complex g.	Zr Calculated g.	Zr Found g.	Zr Difference mg.
5	0.0171	0.0055[8]	0.0055[8]	± 0
5	0.0169	0.0055[8]	0.0055[2]	− 0.06
10	0.0342	0.0111[6]	0.0111[7]	+ 0.01
10	0.0340	0.0111[6]	0.0111	− 0.06
15	0.0513	0.0167[4]	0.0167[5]	+ 0.01
15	0.0510	0.0167[4]	0.0166[5]	− 0.09
20	0.0684	0.0223[2]	0.0223[3]	+ 0.01
20	0.0680	0.0223[2]	0.0222	− 0.12

Anal. Chim. Acta, 21, 34, (1959).

In another series the precipitates were dried at 110°C. for 1 hour and weighed. By calculation using the factor 0.32653, corresponding to the formula Zr_3(Tartrazine) $(OOH)_3$, consistent results were also claimed, shown in Table II, suggesting that direct weighing of the precipitate is feasible. Ions which frequently occur along with zirconium were tested for their reaction with Tartrazine, and sixteen tried gave negative results: Al, Ti, U, La, Ce, K, Cd, Zn, Co, Ni, Cu, Mg, Na, Li, Fe, and Ca. It was noted that the reaction is masked by sulfate and by tartaric or citric acids.

Qualitative tests.—We secured a sample of F.D. & C. Yellow No. 5 Certified (640 Tartrazine) from H. Kohnstamm & Co., Inc., and this was used in all our experiments without purification. In preliminary qualitative tests we confirmed the precipitating action of Tartrazine for zirconium oxychloride and noted the great sensitivity of this reagent to the presence of sulfates. However, we were surprised to find that even a solution containing no sulfates which was made strongly acid with hydrochloric acid gave no precipitate with Tartrazine. This was contradictory to the report by Baiulescu and Turcu but led us to test weaker acid solutions, when precipitation occurred as predicted.

Quantitative tests. *Direct drying at 110°C.*—Quantitative measurements were then begun on three solutions, A, B, and C, prepared to contain 0.400, 0.500, and 0.350 g. ZrO_2/100 ml., respectively. The details of the procedure used were briefly as follows: 50 ml. of the test solution were pipetted into a 250-ml. beaker, diluted with an equal volume of water at about 25°C., then 15 ml. of the 2% solution of Tartrazine were added. The precipitate which formed immediately was allowed to settle, then 10 ml. more dye solution were added to test for completeness of precipitation in the cold, and 25 ml. more after warming on the steam bath to 75°–80°C. After holding overnight at this temperature the supernatant liquor was clear and was

TABLE III

DIRECT WEIGHING OF PRECIPITATE

Drying Conditions	Solution A		Solution B Grams Precipitate/50 ml.		Solution C	
At **100**°C.:						
1 hour	0.5700	0.5821	0.7325	0.7649	0.4905	0.5030
3 hours	0.5504	0.5786	0.7251	0.7352	0.4847	
At **112**°C.:						
1 hour	0.5397	0.5714	0.7115	0.7179	0.4773	0.4816
72 hours	0.5322	0.5635	0.7008	0.7065	0.4705	0.4749

filtered through a weighed Gooch, washing with hot water until a very pale yellow color was obtained. Tests were run in duplicate on each solution, and the residues after washing were dried carefully at gradually increasing temperature in an endeavor to weigh directly without ignition. The results are shown in Table III. It is obvious that the weights at 100°C. were not constant, nor even those at 112°C. (Recommended conditions: 1 hour at 110°C.) The conversion factor given was applied to the values obtained after 1 hour at 112°C. as well as to those maintained at this temperature for 72 hours, with the results shown in Table IV. The values found with this conversion

TABLE IV

APPLICATION OF CONVERSION FACTOR

	Solution A		Solution B Grams Precipitate/100 ml.		Solution C	
At **112**°*C.:*						
1 hour	1.079	1.143	1.423	1.435	0.955	0.963
72 hours	1.064	1.127	1.402	1.413	0.941	0.950
	Using Conversion Factor to ZrO_2					
At **112**°*C.:*						
1 hour	0.352	0.373	0.465	0.469	0.312	0.314
72 hours	0.347	0.368	0.458	0.461	0.307	0.310

factor were not correct, even though the duplicates with Solutions B and C were good checks.

The residues were then heated over a low flame, placed in a muffle furnace at 600°C. for 3 hours, cooled, and weighed. They were replaced in the muffle and held for 1 hour at 1000°C., cooled, and weighed. The results calculated as ZrO_2 are shown in Table V, in comparison with values obtained

TABLE V

TARTRAZINE PRECIPITATE IGNITED TO ZrO_2

Temp. of Ignition	Solution A		Solution B Grams ZrO_2/100 ml.		Solution C	
600°C.	0.417	0.416	0.519	0.519	0.362	0.363
1000°C.	0.400	0.399	0.497	0.499	0.344	0.347
p-hydroxyphenyl arsonic acid						
$ZrO_2 + TiO_2$	0.420	0.420	0.538	0.538	0.389	0.392
TiO_2	0.026	0.026	0.036	0.038	0.045	0.043
ZrO_2 (by diff.)	0.394	0.394	0.502	0.500	0.344	0.349

using our standard method. Hence it was necessary to ignite to secure consistent duplicate results, and when 1000°C. was used, the figures were in good agreement with those found by our usual method and almost identical with the values for the solutions as prepared.

We concluded, therefore, that the use of Tartrazine as a precipitant did not allow direct weighing, but that it showed distinct promise when the precipitate was ignited to the oxide at 1000°C.

Concentration of acid.—In the work described by Baiulescu and Turcu "the pH of precipitation was 1, but precipitation was also complete in stronger acid medium." In view of the results obtained in our qualitative tests we ran a series of precipitations increasing the normality of the solution to which the 2% Tartrazine solution was added. This work was carried out on Solution X which was prepared to contain 0.300 g. ZrO_2/100 ml. In the initial experiments we found a tendency to channel while washing with suction in the Gooch, so we decided to change to a filter paper without suction and to reduce the amount of analytical solution to 25 ml. This was diluted with 100 ml. of water containing the required amount of hydrochloric acid or caustic soda to give the normality desired. Fifty ml. of Tartrazine solution were then added, and the mixture was allowed to stand at 80°C. overnight, filtered and washed with hot water. The results are given in Table VI

TABLE VI

EFFECT OF ACID CONCENTRATION ON PRECIPITATION

SOLUTION X

Normality of Solution	g. ZrO_2/100 ml.
0.1	0.320
0.5	0.324
1.0	0.229
2.0	0.188
4.0	0.030

and indicate that a serious drop in the amount of precipitate occurs as the acid concentration is increased. We then tried to define more exactly the limits of normality within which quantitative precipitation may occur and in these experiments washed with hot dilute acid of the same normality as the final mixture before filtration. The values obtained are indicated on the curve shown in Fig. 1. The general trend is clearly evident and shows a steady reduction in the amount of precipitate as the acid concentration is increased. The upper limit seemed to be in the vicinity of 0.33*N*, and further tests were run to define the lower limit.

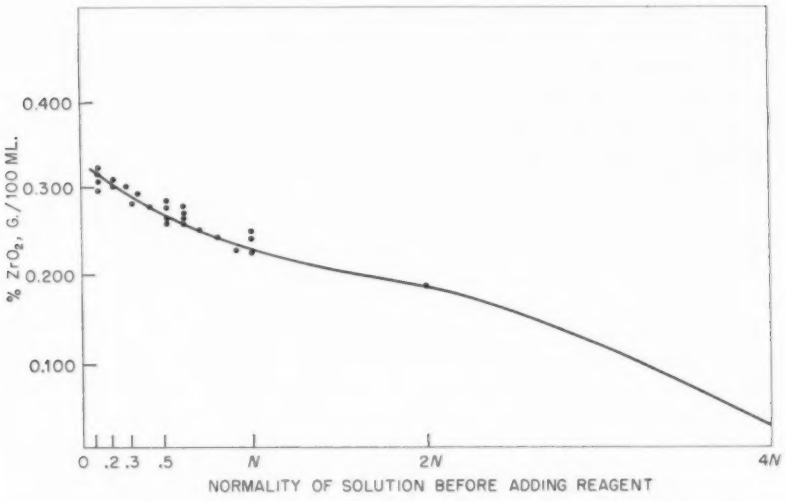


FIGURE 1.—Effect of increasing normality of acid on Tartrazine precipitate from Solution X.

A complicating factor showed up in this series of experiments when it was demonstrated that some TiO_2 was being precipitated along with the zirconium in these lower acid concentrations. This was found quantitatively by fusing the ignited oxides in the usual way, dissolving up, and determining titanium colorimetrically. The first set of results is given in Table VII

TABLE VII

OCCLUSION OF TITANIUM AT LOW NORMALITY OF SOLUTION

SOLUTION X

Normality of Solution	g. ppt./100 ml.	TiO_2 Colorimetrically	ZrO_2 by Difference
0.50	0.266	0.000	0.266
0.33	0.293	0.000	0.293
0.10	0.316	0.015	0.301
0.05	0.329	0.026	0.303
0.02	0.331	0.030	0.301

and was followed up by replicate determinations shown in Table VIII. The values are plotted diagrammatically in Fig. 2 and show that the lower limit for selective precipitation of ZrO_2 was about 0.2*N*. The amount of titanium

occluded is not significant at this or higher normalities, but it becomes appreciable at 0.1*N* and increases at still lower acid concentrations.

TABLE VIII

OCCLUSION OF TITANIUM AT LOW NORMALITY OF SOLUTION

SOLUTION X

Normality of Solution	g. ppt./100 ml.	TiO_2 Colorimetrically	ZrO_2 by Difference
1.0	0.245, 0.245	0.000	0.245, 0.245
0.5	0.286, 0.280	0.000	0.286, 0.280
0.4	0.283	0.000	0.283
0.33	0.299, 0.300	0.003, 0.003	0.296, 0.297
0.3	0.286	0.000	0.286
0.20	0.304, 0.302	0.006, 0.007	0.298, 0.295
0.14	0.304, 0.316	0.009, 0.012	0.295, 0.304
0.10	0.301, 0.314	0.017, 0.019	0.284, 0.295
0.083	0.314, 0.314	0.021, 0.017	0.293, 0.297
0.067	0.323, 0.321	0.022, 0.010	0.301, 0.311

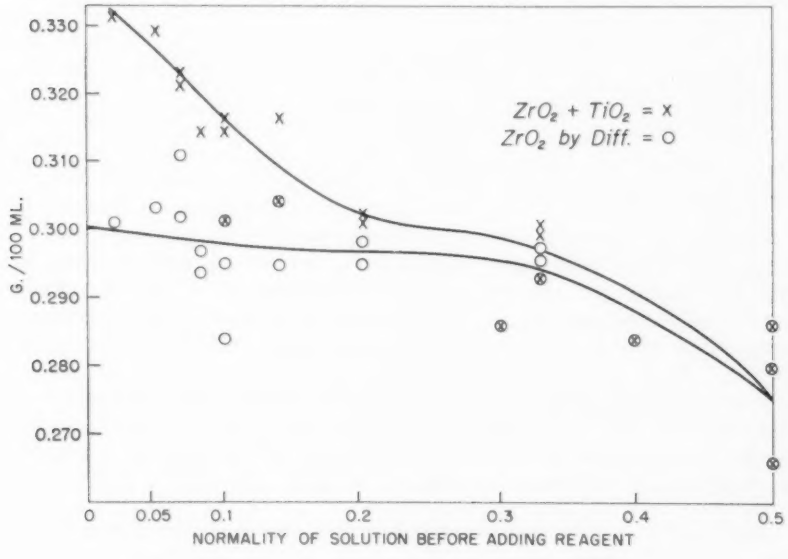


FIGURE 2.—Effect of occlusionTi of O_2 at low normality.

We next endeavored to hold the titanium in solution with peroxide during precipitation of the zirconium with Tartrazine, but this approach was not possible since the peroxide interfered with this precipitation, in some cases preventing it completely.

In reviewing the promising results secured initially on Solutions A, B, and C in the light of this effect of acid concentration we titrated these solutions and found normalities in the range 0.88 to 1.14. With the initial dilution these would fall in the range 0.44 to 0.57*N*, which might be expected to cause low values. However, it should be noted that the first precipitates were washed with distilled water as recommended, while in recent experiments these were washed with the appropriate concentration of acid. To check this point, 25-ml. samples of Solution B were precipitated at an acidity of 0.5*N*, and a direct comparison was run on these methods of washing. The values found by washing with hot water were 0.496, 0.496 g./100 ml., while the corresponding figures with the acid wash were a little lower at 0.492, 0.489. As expected at this acidity, no titanium was occluded in any of these precipitates. In this instance we confirmed the good results obtained initially on washing with water and noted that the figures were appreciably lower when washing with dilute acid. This effect of acid-washing was even more pronounced when precipitating Solution X at 0.5*N*, possibly because the bulk of precipitate was considerably smaller. This experiment demonstrated that when the precipitate is washed with water, the upper limit of acidity may be extended as far as 0.5*N*.

Based on this work on the effect of acid concentration we concluded that (*a*) the minimum value of 0.1*N* recommended (approximately pH 1) is too low, since some occlusion of titanium occurs; (*b*) more accurate values can be obtained by operating in the range 0.2 to 0.5*N* under controlled conditions; and (*c*) when more strongly acid solutions than this are used, precipitation may not be complete.

Conditions of precipitation.—While work on acid concentration was in progress the conditions of precipitation were studied beginning at an acidity of 0.2*N*, allowing the solutions to stand under cold and hot conditions for 1 hour, 4 hours, and overnight before filtration. Washing was carried out with hydrochloric acid of the same normality as the solution after dilution with the reagent. After ignition the oxide residues were fused, dissolved up, and titanium determined colorimetrically. The results are shown in Table IX. They indicate that less titanium is occluded under these conditions when the solution is allowed to remain cold rather than when heated and that there is no merit in letting the solution stand more than 1 hour before filtration.

Effect of silica.—Silica was not included in the original list of cations which may occur along with zirconium, but it is present in the cheaper zirconium tanning materials now commercially available and can also be present in the

ash of leathers given clay as a filler. Preliminary experiments indicated that the presence of silica did not interfere with the use of Tartrazine to precipitate zirconium.

TABLE IX

CONDITIONS OF PRECIPITATION AT ACIDITY OF 0.2*N*

SOLUTION X

Time of Standing	g. ppt./100 ml.	TiO_2 Colorimetrically	ZrO_2 By Difference
Hot precipitation			
1 hour	0.304	0.005	0.299
4 hours	0.304	0.005	0.299
overnight	0.302	0.008	0.294
Cold precipitation			
1 hour	0.302	0.001	0.301
4 hours	0.290	0.001	0.289
overnight	0.293	0.002	0.291

Discussion.—Reviewing the Tartrazine method in the light of the evidence presented here, it is apparent that on further investigation it did not give as clear-cut results as those originally reported. Under the procedures described we could not get consistent figures by direct weighing, and the values were inaccurate using the factor designated. At the minimum acidity specified (pH 1) we found some occlusion of titanium, while precipitation was not complete when the acid concentration was increased over 0.5*N*. However, evidence was obtained that, by adjustment of conditions to control the acidity at the time of precipitation and subsequent ignition of the washed precipitate, Tartrazine is of definite interest for the analysis of leathers containing zirconium. Moreover, the reaction may be carried out at room temperature, and filtration may be begun in 1 hour, so that this can be the basis for a rapid method which is outlined at the end of this paper.

COMPARISON WITH p-HYDROXYPHENYL ARSONIC ACID

The values obtained with Tartrazine under optimum conditions on the whole resemble closely the figures found for the same solutions using p-hydroxyphenyl arsonic acid. In the original form in which this latter method was published any titanium present was held in solution by treatment with peroxide, and the zirconium was precipitated alone by the arsonic acid. This is a good approach when it is desired to determine only zirconium, but in

analyzing some leathers, especially white leathers, we normally wish to determine both TiO_2 and ZrO_2. Hence we prefer to precipitate both together and run TiO_2 colorimetrically. However, we decided to compare the peroxide treatment on some of these solutions. The results obtained are given in Table X and show reasonably good agreement, with very little occlusion of titanium.

TABLE X

p-HYDROXYPHENYL ARSONIC ACID

SOLUTION X

	Grams/100 ml.	
	Standard Method	Peroxide Added
$ZrO_2 + TiO_2$	0.317, 0.324	0.293, 0.298, 0.300
TiO_2	0.027, 0.026	0.003, 0.005, 0.001
ZrO_2 (by diff.)	0.290, 0.298	0.290, 0.293, 0.298

PRECIPITATION WITH SELECTED REAGENTS

Finally we selected some of the preferred methods described in the literature and ran one series of precipitations with Solution B. The results are summarized in Table XI. Further work would be required to make more

TABLE XI

SELECTED REAGENTS

SOLUTION B

Reagent	Grams/100 ml.		
	$ZrO_2 + TiO_2$	TiO_2	ZrO_2
p-hydroxyphenyl arsonic acid	0.538, 0.538	0.036, 0.038	0.502, 0.500
Tartrazine	0.496, 0.496	nil	0.496, 0.496
Mandelic acid	0.507, 0.508	nil	0.507, 0.508
Thiomalic acid	0.521, 0.521	0.021, 0.024	0.500, 0.497

rigorous comparisons. However, when following these procedures as recommended we found some occlusion of titanium with thiomalic acid, but none with mandelic acid. The latter seems to give slightly higher results than those found with p-hydroxyphenyl arsonic acid or with Tartrazine. It was not possible to include p-chloro- or p-bromomandelic acid in this comparison, but the evidence in the literature is that they are superior to mandelic acid.

The trend today is to change from gravimetric methods to those depending

on measurements by specialized instruments. When these are available in research associations and larger laboratories, there can be a marked saving in time without sacrifice of accuracy. However, we believe there is still merit in a good gravimetric method which can be run through simply in the laboratory facilities normally available in progressive tanneries.

OUTLINE OF SUGGESTED METHOD

Weigh accurately 3–5 grams of leather, ash at 600°C., and proceed as described in reference (1) p. 357, fusing, taking up in water, dissolving insolubles in dilute hydrochloric acid, and making up to 500 ml. to constitute Solution B.

Transfer a 25-ml. aliquot to a 250-ml. beaker, add 50 ml. water and 0.5 ml. of 1% phenolphthalein solution, then titrate with *N* NaOH to determine acidity.

Transfer a 50-ml. aliquot to a 250-ml. beaker, and adjust with the calculated amount of standardized caustic soda or hydrochloric acid plus enough distilled water to give 125 ml. solution showing an acidity of 0.33*N*. Add 50 ml. of a 2% solution of Tartrazine at room temperature (25°-30°C.) while stirring, and allow the precipitate to settle for 1 hour. Filter through Whatman #40 paper, and wash with water at room temperature until the filtrate is pale yellow and free from acid. Transfer paper and contents to a weighed porcelain dish, dry, and ignite to constant weight, using a Fisher burner or muffle furnace at 1000°C. for 1 hour. Cool and weigh.

$$\text{Percent } ZrO_2 = \frac{\text{Residue} \times 10 \times 100}{\text{Weight of sample}}$$

ACKNOWLEDGMENT

The authors wish to express their thanks to Miss H. R. Franecke for her assistance in the colorimetric determination of titanium in these experiments.

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DISCUSSION

GENE KIMPEL: If you have occasion to review the leather literature on this subject, you will find that the major contributors have been the authors of this paper. We in the leather field are deeply indebted to them for laying the groundwork for the analysis of zirconium in leather and also for some of the chemistry of zirconium, particularly in view of the fact that zirconium tannages and retannages seem to have become increasingly popular.

I think that they have done a good job in reviewing the different classical gravimetric methods for analyzing for zirconium, and they have evidently evaluated them very well because the method they have come up with, and which the Leather Mineral Analysis Committee is checking, seems to be a very good method, and agreement among the six or seven laboratories that have run the test has been very good.

We are also indebted to Dr. Somerville for keeping a sharp eye on any new methods that come out in the literature.

I think this method he picked out to investigate was interesting in that it mentioned that it was possible to get good results by simply drying the precipitate in an oven and weighing as such. As it turned out, this was not the case. But again I think they should be commended for pursuing the subject further and determining what conditions are necessary for working out a good method for this specific reagent for zirconium.

It was interesting to note that they found that if the acidity was too high, the precipitation was incomplete. And if it was too low, there was occlusion of titanium.

One question I would like to ask: Did you check this occlusion of titanium phenomenon with any of the other cations that might be present in the leather analysis?

DR. SOMERVILLE: We did not check those listed by the original authors, except titanium, because we were naturally most interested in it. We also checked silica, but no others.

MR. KIMPEL: Do you think this method might, if pursued a little further, show some uniqueness in that, since it uses a specific reagent, it might show that it is a little better method than the p-hydroxyphenyl arsonic acid method?

DR. SOMERVILLE: We consider it equally as good, and it might be faster.

LIFE LINES

Brief Biographies of Our Contributors

JOSEPH N. BOYD earned his B.S. in Mathematics at Texas A. & M. College in 1948 and his M.S. in Statistics at the Institute of Statistics of the University of North Carolina in 1950. Formerly chief statistician at the U. S. Naval Mine Defense Laboratory, Panama City, Florida, he has been since September, 1959, a consulting statistician for both the Eastern and Northern Utilization Research and Development Divisions of the U. S. Department of Agriculture. Mr. Boyd is assigned to Biometrical Services, Office of the Administrator, Agricultural Research Service, U. S. Dept. of Agriculture, in Beltsville, Maryland.

IRA D. CLARKE is a graduate of Butler College, Indianapolis, Indiana. He retired in 1957 after 40 years with the U. S. Department of Agriculture, first in the Leather and Paper Laboratory of the Bureau of Chemistry in Washington and from 1941 on in the Hides, Tanning Materials, and Leather Section of the Eastern Utilization Research Laboratory in Philadelphia. An ALCA member since 1920, he has been the author or coauthor of dozens of contributions to *JALCA*. Even in his well-earned retirement he continues to serve us as abstracter of *Das Leder*.

MRS. JEANNE G. FEE is engaged in research on the physical properties of hide and leather at the Eastern Regional Research Laboratory of the U. S. Department of Agriculture. A 1952 graduate of Davis and Elkins College, Elkins, West Virginia, she was on the staff of the National Bureau of Standards for two years before assuming her present position.

DR. EDWARD M. FILACHIONE is Supervisor of the Hide Modification Unit of the Hides, Tanning Materials and Leather Section of the Eastern Utilization Research Branch, U. S. Department of Agriculture. He received his B. S. degree from the University of Illinois and his Ph. D. degree from Northwestern University. After six years of teaching and industrial research he joined the staff of the U.S.D.A.'s Philadelphia laboratory in 1941. His previous research and publications have been primarily in the field of organic synthesis. Since 1951 he has been conducting research in the field of leather chemistry. He joined ALCA in 1955.

EDWARD H. HARRIS, JR. obtained a B.A. degree from LaSalle College, Philadelphia, in 1950. He joined the Eastern Utilization Research Branch, U. S. Department of Agriculture, in 1942 and worked on lactic acid and its

derivatives. In 1951 he was transferred to the unit on chemical modification of hide proteins in the Hides, Tanning Materials and Leather Section.

Dr. Joseph Naghski.—See the February, 1961, *JALCA*.

Ian C. Somerville obtained his B.Sc. and Ph.D. degrees at the University of Edinburgh, Scotland. He has been with the Rohm & Haas Company for thirty years and is head of their Research and Development Laboratory on Leather Chemicals. His contributions to *JALCA* include papers on sulfiting of quebracho, on syntans, and on zirconium tannage. He joined ALCA in 1935 and received the Alsop Award in 1950.

Jesse Wendkos has been associated with the Rohm & Haas Company for thirty years, most of the time in charge of the analytical section of the Leather Chemicals Laboratory. He has been coauthor with Dr. Somerville of several papers on the analysis of zirconium tanning materials and leathers and has served on the Mineral Tannage Committee of our Association for eight years.

Dr. Lee P. Witnauer.—See the February, 1961, *JALCA*.

Russia, we are now told, concentrates to a much greater extent upon the training of engineers than we do here in America. But in Russia practically all the physical scientists are engaged in teaching and research, with almost none going into industry and management. Engineers, on the other hand, are used to a much wider extent in management and administration than they are here in the United States. Whereas in America many chemists, for instance, find occupation in "applied chemistry" with drug concerns and other industrial organizations, in Russia these positions are filled with chemical engineers. In fact, the Russian economy is largely run by people trained as engineers.

—Eric A. Walker. "Engineers and/or Scientists." *Journal of Engineering Education*. Vol. 51, No. 5, Feb. 1, 1961. Reprinted by permission of the American Society for Engineering Education.

Whatever the reason, we seem, here in America, to be turning more and more to physicists and chemists and the like for jobs that involve design and utilization—jobs for which they are not prepared and for which engineers are prepared. A design problem does not become something else simply because we assign it to a scientist rather than to an engineer. Nor does a further multiplication of knowledge eliminate the need to solve the problem. We must recognize that knowledge, in and of itself, is sterile and useless. It becomes important only after it has been put to use in the affairs of man. This is the job for which engineers are specifically trained. This is the work to which they are committed. No one else can do it as well as they.

—Eric A. Walker. "Engineers and/or Scientists." *Journal of Engineering Education*. Vol. 51, No. 5, Feb. 1, 1961. Reprinted by permission of the American Society for Engineering Education.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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FIFTY-SEVENTH ANNUAL MEETING

The Fifty-seventh Annual Meeting of the Association will be held in Washington, D. C., at the Shoreham Hotel, August 20–25, 1961. This will be a joint meeting with the International Union of Leather Chemists Societies.

ABSTRACTS

Mechanical Properties of Wool Keratin and Its Molecular Configuration. M. Feughelman and A. Haly. *Kolloid Z.*, **168** (2), 107–15; abstr. in *J. Soc. Dyers Colourists*, **77**, 40 (1961).—The relationship between the amount of supercontraction at the end of the first and final stages of a wool fiber in concentrated LiBr and the mechanical properties of the fiber at these stages in the LiBr solution is explained in terms of a simple structural model. This requires two types of zones of different thermal stability along the microfibrils in the keratin. One zone, comprising about 36% of the microfibrils, unfolds unimpeded by bulky side chains, and the remaining 64% may be unfolded by overcoming steric hindrance and causing irreversible breakdown of bonds. The model can be used to explain the load-extension behavior and other mechanical properties of single wool fibers. C.L.D.

Study of Leather Breakages by Acoustical Tests. G. Tóth and J. Orkényi. *Bőr- és Cipőtechnika*, **10**, 1–4 (1960); *Hung. Tech. Abstr.*, **12**, 143 (1960).—Leather breakage tests were carried out using 10,000-fold amplification. Fiber breakage was heard distinctly and its crackle could be recorded on tape or photographed by an oscillograph. On the basis of the photographs it was possible to make a comparison of the cross-sectional area of fiber breakages per min. As the load was increased, the cross section of the fiber breakages per min. also increased to a great extent. A phenomenon similar to relaxation was observed following fatiguing of long duration. A direct relation exists between the logarithms of breakage times and breakage loads. Tests show the difference between the fatiguing and the breakage procedures: sections smaller than fiber fascia size break one after the other during the fatiguing procedure while when determining the breakage strength, large numbers of fibers fascia break at an increasing rate.

Surface Tension and Adsorption Studies on Myrobalans Extracts. K. J. Scaria and S. K. Barat. *Bull. Central Leather Research Inst., Madras*, **7**, 147–55 (1960).—Myrobalans nuts were extracted with water and with methanol. The methanol extract was evaporated to dryness and redissolved in water; this extract differed from the aqueous extract by being almost free from salts. The surface tensions of both extracts were measured with a De Nouy tensimeter at concentrations of about 2 to 98 g. solids per l. The surface tension declined with increasing concentration, to a minimum at about 50 g. per l. for the aqueous extract, and at about 60 g. per l. for the methanol extract. Determinations of adsorption on charcoal showed that adsorption increased with concentration to maxima that agreed very roughly with the surface tension minima; the aqueous extract adsorption curve gave a second, unexplained maximum at still higher concentrations. Analyses of the solutions showed that very little nontannin was adsorbed. These data indicate that myrobalans tannin acts like a typical association colloid, with a critical micelle concentration of about 12 g. solids per l. H.B.M.

A Note on the Demineralization of Sharkskins. D. R. Krishnan and S. K. Barat. *Bull. Central Leather Research Inst., Madras*, **7**, 163 (1960).—The collagen of sharkskin is more sensitive to acid and alkali than mammalian collagen. The calcareous horny layer of sharkskin can be removed in 1–1.5 hr. by treatment with saturated NaCl solution containing 20% of concentrated HCl (sp. gr. 1.19) without damaging the skin proper. The solution can be reused repeatedly. The skins are neutralized with $NaHCO_3$ in saturated brine. H.B.M.

Manufacture of Shrunken Grain Kid Leather from Goatskin with Indigenous Tanning Materials. J. C. Deb, P. Ramakrishnan, and Y. Nayudamma. *Bull. Central Leather Research Inst., Madras*, **7**, 156–62 (1960).—Large or damaged goatskins, not suitable for glazed kid, are well opened up by drastic liming (in paint 2 days followed by liming for 6 days) and bating (overnight, ending at 100°F.). The bated skins are beamed on the flesh side to remove excess water. Shrinking is done with a mixture of myrobalans powder, myrobalans extract, salt, and formic acid, in a heated drum (100°F.). The salt is added first, then the skins, then the myrobalans powder, and then the extract and formic acid in 30% float. After 3 hr. the skins are washed, horsed, and Cr tanned. After shaving, the skins are bleached with oxalic acid, neutralized, fatliquored, struck out by hand, oiled on the grain side and dried. Procedures are given for finishing with resin-wax finish or with a glazing finish. H.B.M.

Facts Regarding the Paste-Drying of Box Sides. H. Schmid. *Tanner* (India), **15**, 215–17 (1960).—Use of various proprietary materials in Cr tanning, neutralizing, retanning, and fatliquoring is described. It is stated that cod oil products have an adverse effect on tightness of pasted leather. The milder the drying conditions, the fuller the leather. Ideally, drying conditions should be so regulated as to maintain a "hygroscopic equilibrium" corresponding to a water content that is 3% or 4% below the actual water content of the leather at the moment. H.B.M.

Neutral Salt-free Basic Chromium Salts and the Use of Anion Exchangers for Their Preparation. K. H. Gustavson. *J. Soc. Leather Trades Chemists*, **45**, 9–16 (1961).—Hydroxyl-charged anion-exchange resins were used to prepare solutions of basic chromium salts free from neutral salts. All the hydroxyl groups supplied by the resin exchanged with the anion present in the chrome salt. The amount of the resin calculated to give the desired basicity was added gradually to a solution of the 100% acid chrome salt. Up to 40% basic chrome chlorides, perchlorates, and sulfates may conveniently be prepared in this way. The preparation of 65–75% basic chrome chlorides and perchlorates is feasible under favorable conditions. S.D.

Developments in Combination Tannages. II. Some Factors Which Influence the Storage Stability under Normal Conditions. R. L. Sykes and D. A. Williams-Wynn. *J. Soc. Leather Trades Chemists*, **45**, 16–26 (1961).

—In this study factors that effect deterioration of chrome retan leathers stored up to 9 months at 21°C. and 65% R. H. were investigated. Wattle, quebracho, and sumac retannages caused about equal loss in buckle tear strength of chrome retan goatskins after 3 months of storage. The strength was reduced to 77–85% of the initial strength. The corresponding values for a syntan retannage (Orotan TV) and for the straight chrome were 92% and 97%. Increasing the amount of retannage in general caused a more rapid rate of deterioration. The use of masking agents in the tannages produced leather with greater strength and better stability. The results generally support the theory that deterioration is caused by liberation of strong acid from the chromium-pelt complex by the vegetable tannins. However, it is pointed out that further investigations are required before this theory can be considered proved.

S.D.

PATENTS

Water-repellent Composition Containing Organopolysiloxane and Organotitanate, and Leather Treated Therewith. U. S. Pat. 2,970,126. E. D. Brown, Jr., Schenectady, N. Y., assignor to General Electric Company, a corporation of New York. Filed June 12, 1958.—1. A composition for the waterproofing of leather comprising, by weight, (1) from about 9 to 19 percent of a material comprising the product of intercondensation at temperatures of from about 100°C. to 150°C. of a mixture of ingredients composed essentially by weight of (A) one part of a cohydrolysis product of a mixture of ingredients consisting essentially of (*a*) a trialkyl hydrolyzable silane wherein the fourth valence of the silicon atom is attached directly to a hydrolyzable group, and (*b*) an alkyl silicate, the alkyl groups of the silane and silicate containing at most four carbon atoms, and said cohydrolysis product containing a plurality of silicon-bonded hydroxyl groups, there being employed a molar ratio of from about 1 to 2 mols of the alkyl silicate per mol of trialkyl hydrolyzable silane, and (B) from 0.5 to 6 parts of a linear high viscosity organopolysiloxane fluid of above 200,000 centipoises viscosity and containing terminal silicon-bonded hydroxyl groups, the organic groups being attached to silicon by carbon-silicon linkages and being selected from the class consisting of monovalent hydrocarbon radicals and halogenated aryl radicals, there being present an average of about two organic groups per silicon atom in the organopolysiloxane fluid, said intercondensation proceeding through the medium of the silicon-bonded hydroxyl groups of (A) and (B), (2) from about 9 percent to 19 percent of a curable hydrolysis product having the formula

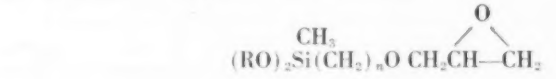
$$R_mSiO_{\frac{4-m}{2}}$$

of a mixture of hydrolyzable lower alkyl silanes, where R is a member selected from the group consisting of lower alkyl groups and mixtures thereof, and *m*

is a number from 1.1 to 1.8, (3) from about 24 percent to 34 percent of a compound of the general formula $(R'''O)_4Ti$, where R''' is selected from the class consisting of alkyl groups having less than about 13 carbon atoms per molecule and mixtures thereof, and (4) from about 38 percent to 48 percent of a solvent.

Sheet Comprising Leather Fibers, Ethylene Oxide-Dicyandiamide Condensation Product and Rubber Latex and Process for Preparing Same. U. S. Pat. 2,948,692. D. K. Pattilloch, New York, and C. Polowczyk, Elmhurst, N. Y., assignors to Michigan Research Laboratories, Inc., Long Island City, N. Y., a corporation of Michigan, and Electro-Chem Fiber Seal Corporation, New York, N. Y., a corporation of Delaware. Filed May 1, 1957. —1. The process of producing a leather sheet comprising the steps of forming an aqueous suspension of shredded leather fiber, adding an ethylene oxide-dicyandiamide condensation product to said suspension, thereafter adding to the suspension a curable elastomeric latex selected from the group consisting of polymers of 2-chloro-1,3-butadiene and natural rubber, forming the suspension into a sheet and curing the elastomer.

Method of Tanning Hide. U. S. Pat. 2,970,881. R. W. Alsgaard and J. W. Gilkey, Midland, Mich., assignors to Dow Corning Corporation, Midland, Mich., a corporation of Michigan. Filed Dec. 15, 1958.—1. A method of preparing leather which comprises contacting hide with an aqueous dispersion of an organosilicon compound of the formula



in which R is an aliphatic hydrocarbon radical of less than 4 C atoms and n in an integer of from 2 to 3 inclusive, at a pH of at least 9 until the hide is suitably tanned, the organosilicon compound being present in amount of at least 10% of the dry weight of the hide.

Treatment of Montan Wax with Chromic Acid and Simultaneous Formation of Chromic Tanning Mash. U. S. Pat. 2,971,813. A. Sentek, Swierczewskiego-street 149, m.104, Warsaw, Poland. Filed Oct. 4, 1957.—5. A method for improving montan wax comprising the steps of dispersing montan wax in an aqueous solution of nitric acid having a concentration of about between 40–50%, so as to cause an exothermic reaction between said montan wax and said aqueous nitric acid, thereby raising the temperature of the thus formed reaction mixture; allowing said mixture to react for a period up to one hour while preventing the temperature thereof from rising above about 80°C.; cooling said reaction mixture so as to substantially terminate said reaction; separating the thus treated montan wax from the remainder of said reaction mixture; subjecting said separated montan wax to the action of an oxidizing agent selected from the group consisting of chromic acid and bichromates, so as to improve the quality of said montan wax and simul-

taneously to form a chromic tanning mash; separating the thus treated montan wax from said tanning mash; and spray drying the thus separated tanning mash so as to transform the same into a powdery dry substance.

Tanning with Alkaline Glyoxal. U. S. Pat. 2,971,814. L. Seligsberger, Newton Center, Mass., assignor to the United States of America as represented by the Secretary of the Army. Filed Dec. 23, 1957.—1. In the production of leather, the process of immersing a hide in an alkaline aqueous salt solution having a pH of about 9 to about 10.5 until chemical equilibrium between said salt solution and said hide has been reached, the concentration of said salt solution being about 1–2.5 N, then adding glyoxal to said salt solution, lowering the pH of said hide after tannage has been effected by treating said hide with an acidic liquor prior to rinsing and drying said hide, until said hide is stabilized at a pH of not more than about 7, and drying the tanned stabilized hide; whereby a full, strong and pliable leather having a grain structure substantially free from swelling and cracking is obtained.

Partial Dyeing of Fur Skins and Leather. U. S. Pat. 2,969,271. O. Markgraf, Neckargemund, C. Schuster, K. Herrle, and E. Boehm, Ludwigshafen (Rhine), and E. Schaefer, Mannheim, Germany, assignors to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany. Filed May 21, 1957.—1. A process for the partial dyeing of fur skins and leather with dyestuffs for fur skin and leather which process comprises partially covering the material to be dyed selected from the group consisting of fur skins and leather with a polymer which has been prepared from at least 20% by weight, with reference to the weight of total polymer, of a N-vinyl lactam having at least 8 carbon atoms in the molecule, which polymer is insoluble at elevated dyebath temperatures and soluble at lower temperatures, drying the thus partially covered material to be dyed, dyeing the same at a temperature sufficiently high to keep the polymer in the water-insoluble state, and washing the dyed material in an aqueous bath at a temperature at which the applied polymer is soluble to remove said polymer and thus obtain the partially dyed product.

Process for Tanning Leather. U. S. Pat. 2,970,031. D. E. Nagy, Stamford, Conn., assignor to American Cyanamid Company, New York, N. Y., a corporation of Maine. Filed Aug. 31, 1955.—1. A process for tanning leather which comprises first soaking pickled hides in a water solution of a mineral tanning agent and then impregnating the resulting hides containing said mineral tanning agent with an aqueous alkali metal cyanate solution until a quantity of alkali metal cyanate has been absorbed sufficient to set the mineral tanning agent therein and convert the hides into leather.

Stable Solutions of Compounds of Tannins with Boric Acid. U. S. Pat. 2,970,032. O. C. Jekel, 1 Freihammerstrasse, Salzburg-Obergnigl, Austria. Filed May 27, 1957.—1. A tanning solution comprising a substantially stable clear solution of a tannin-boric acid compound in an equilibrium solvent mix-

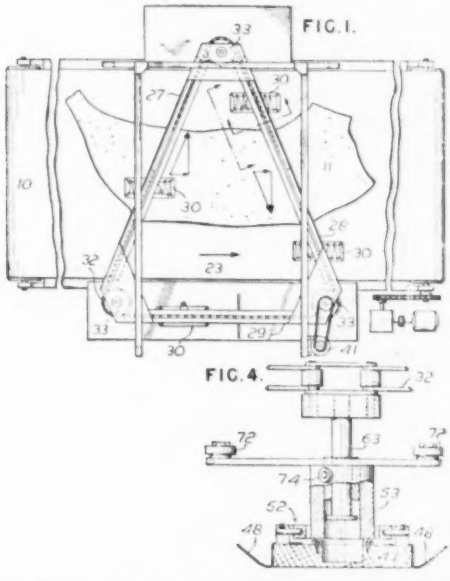
ture of ethyl acetate, ethyl alcohol, acetic acid and water in such proportions as to satisfy the equation

$$\frac{\text{(Molar concentration of acid)} \times \text{(molar concentration of alcohol)}}{\text{(Molar concentration of ester)} \times \text{(molar concentration of water)}} = 1/4$$

the quantity of acetic acid in said equilibrium solvent mixture not exceeding 4%.

Process of Tanning Leather and Product thus Produced. U. S. Pat. 2,970,033. F. A. Edmonds, Arlington Heights, and R. P. Doyle, Chicago, Ill., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine. Filed Sept. 6, 1957.—1. A process for tanning leather comprising soaking hides in an aqueous tanning liquor containing between about 0.5% and 10% by weight of dicyandiamide, between about 0.5% and 10% by weight of a water-dispersible methylated melamine-formaldehyde resin and between about 0.5% and 20% by weight of a lignosulfonate at a temperature between about 60°F. and 160°F. and at a pH between about 3 and 6 until said hides are tanned, said percentages being based on the weight of said hides.

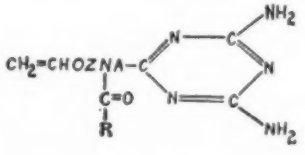
Cleaning Hides. Brit. Pat. 840,600. Swift & Co. Filed Dec. 27, 1957.



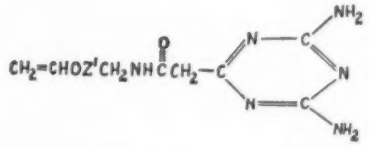
Apparatus for swabbing the horizontal surface of articles such as hides, to remove surplus liquid therefrom comprises a conveyer for transporting the

articles along a horizontal path and power actuated means for moving a swab or swabs repeatedly over, and at least partially across, the conveyer along a horizontal path inclined to the direction of movement of the conveyer, the direction of movement of each swab being such as to give it a component of movement in the direction of movement of the conveyer. In the apparatus shown in Fig. 1, an endless belt conveyer 10 carries hides 11 in the direction of arrow 23. A triangular frame having sides 27, 28, 29, formed of angle irons, carries an endless chain 32 round sprockets 33 at the corners of the triangle, one of the sprockets being driven by motor 41. Swabs 30, attached to the chain, traverse the conveyer while passing along sides 27 and 28, the resultant movement of the swabs with respect to the hides being normal to the direction of movement of the hides. Each swab comprises a wooden block 47 (Fig. 4), with metal wings 48 over which a padded fabric covering is laced. The block 47 is mounted on gimbals 52 and on a cylindrical body 53 in which slides a pin 63 attached to the chain 32. Guide bearings 72 co-operate with side plates of the triangular frame to maintain the alignment of the swabs and a cam follower 74 on the body 53 co-operates with cams on the sides 27 and 28 of the frame to raise the swab just prior to the point at which it passes above the conveyer and to lower it on the articles to be cleaned just prior to the middle of the conveyer. In a modification (Fig. 6, not shown), the frame comprises two horizontal portions inclined to the direction of movement of the conveyer, a separate endless chain on each portion to which is attached a swab which is lowered on the articles on the conveyer during its motion from the centre of the conveyer toward the edge, and is raised out of contact with the articles during return to the centre of the conveyer. The two swabs operate one on either side of the centre line of the conveyer.

Waterproofing. Brit. Pat. 840,169. Rohm & Haas Co. Filed Nov. 16, 1956. —Water-repellent finishes are obtained on textiles, paper and leather by treatment with aqueous dispersions of copolymers of vinyl compounds and guanamines of the formula

I 

or

II 

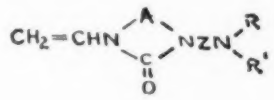
where A is $—CH_2CH_2—$, $—CH(CH_3)CH_2—$ or $—CHR^1—$; R is H, $C_1—C_{18}$ alkyl, $C_6—C_{10}$ aryl (including halo-aryl), $C_1—C_4$ alkoxy, benzyloxy or alkoxyalkyl of 1—4 carbon atoms in each part; R^1 is H or $C_1—C_8$ alkyl; Z is $C_2—C_6$ alkylene; and Z^1 is $C_1—C_5$ alkylene; if R is H the acylated N atom must be flanked by two $—CH_2—$ groups in Z and A respectively. Specified copolymers

are those from (1) butyl acrylate and β - [N - (β - vinyloxyethyl)-palmitamido]-propioguanamine; and (2) lauryl acrylate and 2 - [N - (6 - vinyloxyhexyl)-carbamylmethyl]-4:6-diaminotriazine.

It is also stated that the monomer (1) above gives a water-repellent finish on leather.

Process for Increasing the Water Resistance of Leather. U. S. Pat. 2,968,580. J. Plapper and R. Heyden, Dusseldorf, Germany, assignors to Bohme Fettchemie G.m.b.H., Dusseldorf, Germany, a corporation of Germany. Filed June 25, 1958.—1. The method of water-proofing leather which comprises impregnating tanned leather with a water-miscible derivative selected from the group consisting of esters, amides and acids of a polybasic acid selected from the group consisting of dibasic and higher polybasic organic acids and tribasic and higher polybasic inorganic acids, said derivative containing at least one hydrophobic radical and at least two salt-forming radicals capable of forming complexes and thereafter impregnating said tanned leather with a water-miscible, cationic-active, organic, complex salt of a polyvalent metal containing a ratio of at least 2.5 mols of an alcohol-soluble, basic salt of a polyvalent metal, with one mol of an acid ester of phosphoric acid esterfied with an alcohol containing a hydrophobic radical, said alcohol having about 6 to about 18 carbon atoms, and having coordinated with said basic salt and said acid ester a lower molecular weight alcohol.

Resin-treated Paper or Paper Pulp; Waterproofing; Making Leather. Brit. Pat. 838,817. Rohm & Haas Co. Filed Sept. 5, 1956.—Compounds of the formula



where A is C_2—C_3 alkylene, R and R' are H, C_1—C_{18} alkyl, C_2—C_{18} alkenyl, phenyl, benzyl or cyclohexyl, or with the N atom form a morpholine, piperidine or pyrrolidine ring (not further substituted) and Z is C_2—C_{18} alkylene (optionally substituted by phenyl or vinyl) or cycloalkylene, are used as follows: (1) as water-repellent finishes on textiles or leather; 1-(β-octadecylaminoethyl)-3-vinyl-imidazolidin-2-one is mentioned as suitable; (2) as components (in monomeric or polymeric form) of urea- or melamine-formaldehyde resins used to modify paper, such resins being after-cured; (3) polymers and co-polymers of compounds (R = R' = H) are useful additives to paper pulp to increase the wet strength, especially if reacted with formaldehyde and/or after-cured; suitable for this purpose are (a) poly-1-(β-amino-ethyl)-3-vinyl-imidazolid-2-one used in conjunction with a conventional urea-formaldehyde resin; and (b) poly-1-(β-aminoethyl)-3-vinyl-hexahydropyrimidin-2-one; (4) poly-1-(β-octadecylaminoethyl)-3-vinyl-imidazolidin-2-one gives a soft flexible effect on leather; (5) poly-1-(β-dicyclohexylamino-ethyl)-3-vinyl-hexahydro-pyrimidin-2-one provides a water-repellent coating on leather.

Dyeing of Leather. U. S. Pat. 2,967,751. C. Streck, Loudonville, N. Y., assignor to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware. Filed May 31, 1957.—1. A process for dyeing leather on one side comprising spraying such leather with an aqueous alkaline bath consisting essentially of an aqueous alkaline solution of (in about equivalent amounts) an ice color coupling component devoid of solubilizing groups and an ice color diazoamino component which is an ice color diazo compound devoid of solubilizing groups, which compound has been solubilized and stabilized against azoic coupling on the alkaline side by reaction with an organic amine containing at least one solubilizing group and at least one replaceable hydrogen atom attached to an amino nitrogen atom, and then developing the ice color on the leather by treatment with an acidic material.

Waterproofing Leathers. Brit. Pat. 839,360. Clark Ltd., C. & J. Filed Oct. 12, 1956.—Tanned leather is waterproofed by treatment with dispersions or solutions, for example in isopropanol or methanol, of primary or secondary aliphatic amines having at least 12 C atoms, such as stearyl-, dodecyl-, or dioctylamine, together with a cross-linking agent such as formaldehyde, glyoxal, or crotonaldehyde, which binds the amine to the leather. The two materials may be used together or in succession and with or without an acid or an alkaline catalyst such as sulphuric acid or caustic soda. Treatment is effected with moderate heating, e.g. to above 50°C.

Coated Fabrics or Leather. Brit. Pat. 839,377. Ciba Ltd. Filed Aug. 16, 1956.—Fabrics or leather are coated or impregnated with polymers containing hydrazide groups or derivatives thereof which are made by reacting hydrazine or its hydrate with a polymer which contains carboxylic acid ester groups as the sole groups capable of reacting with hydrazine, whereby at least a part of the ester groups, is replaced by hydrazine groups and the final product contains, besides hydrazide groups, unreacted ester groups incapable of reacting with hydrazine and, if desired, reacting the hydrazide groups with compounds capable of doing so. Polymers specified are those of acrylic and methacrylic esters and copolymers of such esters (*see* Group IV (a)). Examples (3), (4), (6), (7), (19), (20) and (21) illustrate the application of the above polymeric materials to fabrics made from cotton or viscose and Example (17) illustrates a leather coating process.

Organic Mercury Compositions. U. S. Pat. 2,958,625. R. Rebold, Ossining, N. Y., assignor to Gallowhur Chemical Corporation, a corporation of New York. Filed Sept. 29, 1958.—1. A stable highly concentrated organic mercury composition comprising the following constituents in approximately the following proportions, by weight:

	Grams
Phenylmercury acetate	336
Monoethanolamine	61
Polyoxyethylene sorbitan monolaurate	56
Water	107

In treating leather imparts bactericidal and fungicidal properties.

Coated Fabrics; Waterproofing; Paper. Brit. Pat. 840,891. Rohm & Haas Co. Filed July 6, 1956.—Carbamato-ethers and thioethers containing a vinyl group (*see* Group IV (b)), their N-methylol and N-(C_1—C_4 alkoxy) methyl derivatives, and their polymerization, co-polymerization, and condensation products are used in impregnating and coating compositions for paper, wood, leather, fibres, fabrics, and other materials. The monomers in which the nitrogen of the carbamato group is attached to one or two hydrogen atoms may be applied to cellulosic materials such as paper, cotton, or rayon, and caused to react therewith so as to introduce groups capable of reacting with styrene, acrylamide, acrylo nitrile, acrylates, and other ethylenically unsaturated compounds, whereby the water-repellency, stiffness, and other properties of the materials are modified. The monomers may be used for modifying urea-, thiourea-, and melamine-formaldehyde resins and these modified resins may be used for treating paper, fabrics, wood, and leather. These materials may be coated with the homo- or co-polymers by application of solutions or emulsions. Fabrics and fibres of wool and nylon may be treated. The coatings or impregnations may be subjected to heat or other curing treatments. In examples: (1) vinylthioethyl carbamate is converted into a methylol derivative by treatment with aqueous formaldehyde and applied by brushing or dipping to fabrics, fibres, or other articles. The coated material is dried and cured by heating. It may then be bonded to polyester-vinyl type resins applied as solutions and then dried and cured to form sheets with firm adhesion between substratum and resin; (25) an aqueous solution of the polymethylol derivative of polymerized vinylthioethyl carbamate is added to paper pulp in a beater, the pH is adjusted to 4.0 and the pulp is made into paper having a high wet-strength; the polymer solution is added to rubber latex, rayon tyre cords are dipped in the mixture and air dried and incorporated in tyre carcases which are then heat cured; (28) a polymer obtained from a mixed N-*tert.* alkyl vinyl-thio-ethyl carbamate in which the alkyl group has an average of 13 carbon atoms is dissolved in xylene, the solution is emulsified in water, and the emulsion is applied to cloth which, after drying, becomes water-repellent; (36) a copolymer of butyl methacrylate, carbamyl chloride, morpholine and 5-(hydroxypentyl) vinyl ether is used as a binder in a clay or clay-titania composition for coating paper and paper-board.

Coated Leather. Brit. Pat. 838,754. Deutsche Gold- Und Silber-Scheideanstalt Vorm. Roessler. Filed May 6, 1958.—Leather having a fat content of more than 10% is initially coated or brushed with an aqueous dispersion containing natural or synthetic rubber (e.g. polychlorobutadiene), the coating is dried and the coated leather thereafter treated in known manner with an adhesive.

Unhairing Skins. Brit. Pat. 837,521. Realisations Ultrasoniques. Filed June 27, 1958.—A process for unhairing skins comprises the steps of submitting the skins to a swelling operation in water containing a wetting-agent and an antiseptic and thereafter treating the skins by means of ultrasonic waves at a frequency lower than 100 kc/s. In an example, dry skins are soaked in water containing a wetting-agent and an antiseptic for at least 50 hours. The skins are slightly dried and treated with ultrasonic waves at a frequency between 10–100 kc/s. for about 3 minutes in a water tank.

Treating Leather with Polyethers in the Presence of Polyfunctional Isocyanates. Brit. Pat. 837,356. Imperial Chemical Industries Ltd. Filed Jan. 16, 1959.—Leather is impregnated with polyethers in the presence of polyfunctional isocyanates. The polyether may be linear or branched. Specified polyethers are polytetramethylene glycol and polypropylene glycol and the polymers and copolymers of ethylene oxide, propylene oxide, epichlorhydrin, oxacyclobutane, tetrahydrofuran and substituted oxacyclobutane. Specified isocyanates are tolylene-2:4-diisocyanate, mixtures of tolylene-2:4 and 2:6- diisocyanates, p:p^1-diisocyanato-diphenylmethane, diphenyldiisocyanate, dimethyldiphenyl diisocyanate, naphthalene diisocyanate and hexamethylene diisocyanate. Between 0.5 mol. and 4 mol. and preferably between 1 and 2 mol. of polyfunctional isocyanate is used per mol. of polyether. The leather may be first treated with the polyether then with the polyfunctional isocyanate or impregnated with a mixture of polyether and isocyanate or with a prepolymer made by interacting a polyether with isocyanate in conjunction with further isocyanate. The leather may be de-aerated before impregnation and the impregnation may be carried out under pressure. The polymer is cured by heat-treatment and/or by treatment with a catalyst.

I think it is only fair to say that most pure scientists have themselves been devastatingly ignorant of productive industry, and many still are. It is permissible to lump pure and applied scientists into the same scientific culture, but the gaps are wide. Pure scientists and engineers often totally misunderstand each other. Their behaviour tends to be very different: engineers have to live their lives in an organized community, and however odd they are underneath they manage to present a disciplined face to the world. Not so pure scientists. In the same way pure scientists still, though less than twenty years ago, have statistically a higher proportion in politics left of centre than any other profession: not so engineers, who are conservative almost to a man. Not reactionary in the extreme literary sense, but just conservative. They are absorbed in making things, and the present social order is good enough for them.

—C. P. Snow. *The Two Cultures and The Scientific Revolution.* Cambridge University Press, 1959.

Pure scientists have by and large been dimwitted about engineers and applied science. They couldn't get interested. They wouldn't recognize that many of the problems were as intellectually exacting as pure problems, and that many of the solutions were as satisfying and beautiful. Their instinct—perhaps sharpened in this country by the passion to find a new snobbism wherever possible, and to invent one if it doesn't exist—was to take it for granted that applied science was an occupation for second-rate minds.

—C. P. Snow. *The Two Cultures and The Scientific Revolution.* Cambridge University Press, 1959.

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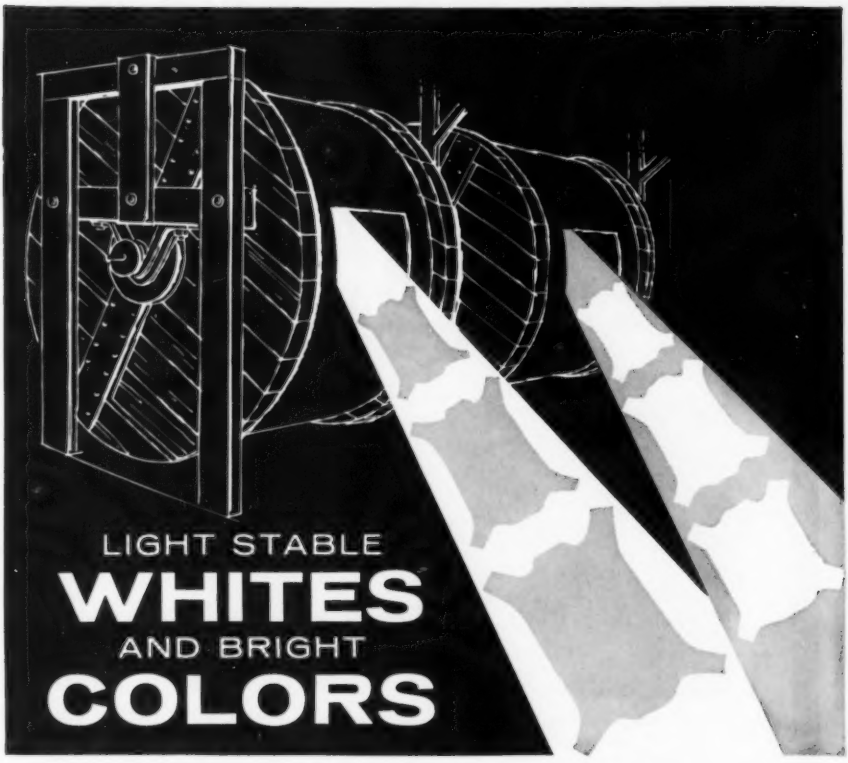

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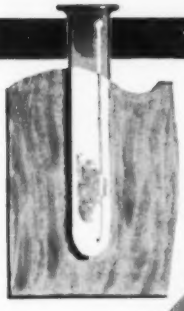

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In Canada: Tennant & Michaud, Ltd., Toronto and Montreal

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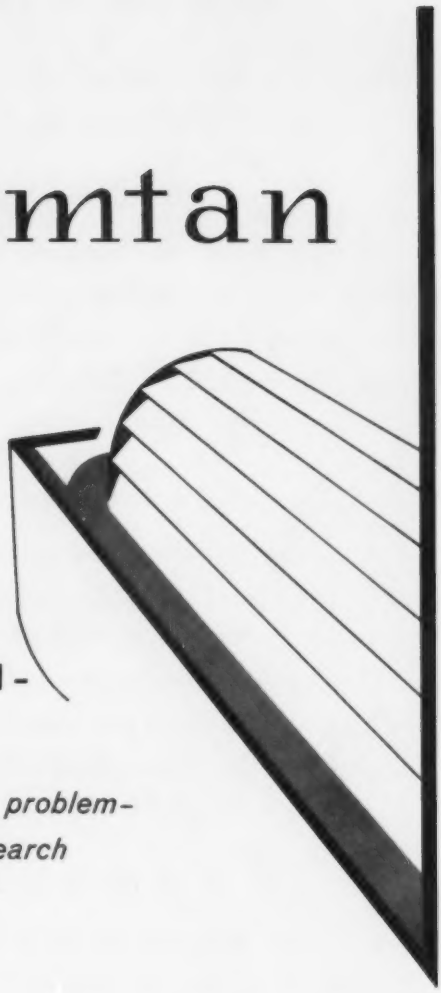

unhairing -
bating -
sewage control -

.....whatever the problem-
Chemtan research
is involved !

from soak to finish -

CHEMTAN COMPANY, INC. EXETER, N. H.